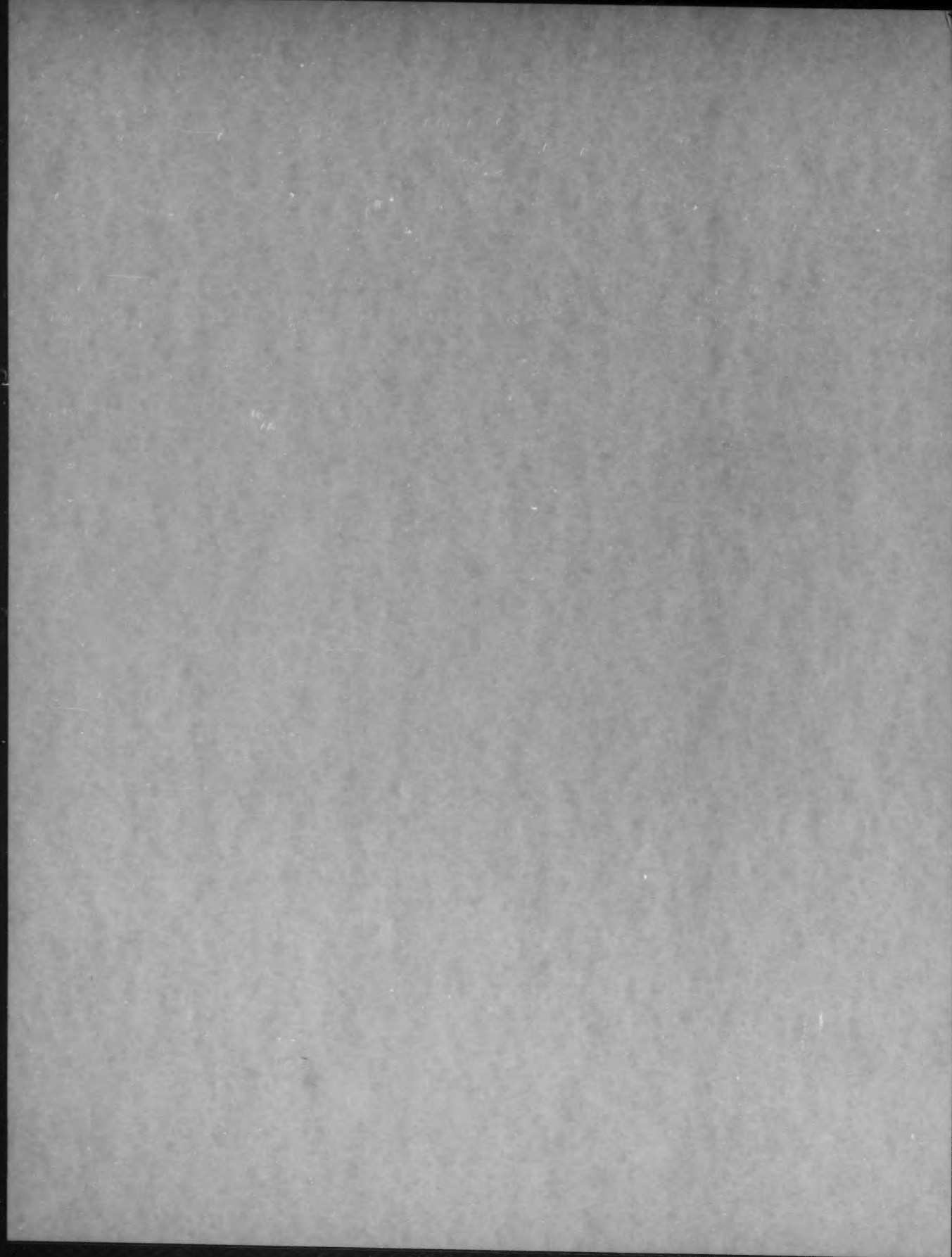


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TOWARD NEW SUCCESSES OF SOVIET CHEMISTRY

The publication of that work of genius by Comrade Stalin "Economic Problems of Socialism in the USSR", and the recent XIX Congress of the Communist Party of the Soviet Union have been great events in the life of our country. The resolutions and the agenda of the XIX Party Congress, and Comrade Stalin's speech, which was a fighting program of action, of great historical and international importance, inspire the Party and the whole Soviet nation to engage in the most self-denying struggle for new triumphs in the building of communism.

Comrade Stalin's work "Economic Problems of Socialism in the USSR" is devoted to the discussion of the most basic problems of the political economy of socialism. In it Comrade Stalin presents in plain and convincing language the economic laws of socialism, and determines the basic conditions for the gradual transition from socialism to communism. The discovery by Stalin of the basic economic laws of socialism is of the utmost importance. "The most vital features and requirements of the basic economic law of socialism", declares Comrade Stalin, "might be formulated more or less in the following way: the assuring of the maximum satisfaction of the constantly growing material and cultural demands of the whole community by means of the continuous growth and improvement of socialist production based on higher technology".^{*} This definition reveals the very essence of socialism. In order to achieve the actual transition from socialism to communism Stalin pointed to the necessity of achieving three basic preliminary conditions. First the continuous growth of social production must be assured, with particular stress on the production of means of production. Second it is necessary, by gradual steps, achieved at a rate acceptable to the kolkhozes, and hence to the community as a whole, to elevate kolkhoz property to the level of national property generally, and to convert commerce into a barter system. Finally, a cultural level of the community must be achieved such that all of its members are assured of the possibility of full development of their physical and intellectual capabilities.

The realization of the conditions pointed out by Stalin in his work is the task of the entire Soviet nation, which is triumphantly building communism under the leadership of the Communist Party, under its great leader and teacher Comrade Stalin.

Among the resolutions of the XIX Party Congress was the following: "The chief tasks of the Communist Party of the Soviet Union now are to build up a communist society by gradual transition from socialism to communism; continuously to raise the material and cultural level of the community; to bring up the members of the community in a spirit of internationalism and brotherly relations with the workers of all countries; and in every way to strengthen the active defence of the Soviet Fatherland against the aggressive acts of its enemies."^{**}

There can be no greater privilege for Soviet scientists than to take the most active part in this great undertaking. The chief duty of Soviet chemists is to contribute to the continuous growth of communal production, and to the raising of the general cultural level of the community.

The directives of the XIX Congress relating to the Five-Year Plan for the development of the USSR contain the basic points of Stalin's work on economic problems. The Five-Year Plan for 1951-1955 is a great new step forward on the path of our progress toward communism.

Great and responsible tasks confront Soviet chemists who are engaged in the fulfilment of these directives. It will suffice to point out that the growth in the production of some of the most important chemicals is of the following order: caustic soda 79%, soda 84%, mineral fertilizers 88%, synthetic rubber 82%, cement 120%. A

^{*} L. Stalin, *Economic Problems of Socialism in the USSR*, State Political Press, 1952, p. 40.

^{**} "Statute of the Communist Party of the Soviet Union". "Pravda" 1952, 1.

large increase in production of non-ferrous metals is envisaged, as follows: refined copper by 90%, lead 2.7 times, aluminum not less than 2.6 times, zinc 2.5 times, nickel by 53%, and tin by 80%.

In connection with the projected increase in power supply during the current Five-Year Plan, resulting from the completion of such hydroelectric stations as that of Kuibyshev, Gorki, and Ust-Kamenogorsk, and in particular from the commencement of work on the exploitation of the power resources of the Angara River, the question of the use of local sources of raw materials for the aluminum, chemical, and other industries will arise.

The Five-Year Plan envisages considerable increase in the capacity of primary oil refineries, and of the fuel gas industry. The wider use of gas is intended, both for domestic purposes and as an automobile fuel, and as a source of chemical raw materials. The directives mention the importance of plant production for the needs of chemical industry.

Chemical industry is charged with the rapid and considerable increase of the mineral fertilizers, the soda, and the synthetic rubber industries. Special stress is laid on the general development of the synthetic rubber industry based on the use of gaseous petroleum products.

Apart from basic chemicals, the Plan envisages increase in the production of plastics, dyestuffs, raw materials for the rayon industry, and a widening of the assortment of other chemicals. Considerable tasks also confront the paper, the wood chemical, and the hydrolytic industries.

The continuous growth in socialist production, and the raising of the productivity of the work of the community, should raise the national income of the USSR during the five years by not less than 60%.

The directives impose special tasks on Soviet scientific institutions: "To improve the work of the scientific research institutes and of the higher educational establishments, and to make fuller use of scientific resources for the solution of the more important problems of development of the national economy, for the generalization of research results, and for the wider practical application of scientific discovery. In every way to collaborate with scientists in the development of their theoretical problems in all domains of knowledge, so as to strengthen the bonds between science and industry".*

G. M. Malenkov, in reading the report of the Central Committee to the Congress, showed that in the struggle for further technical progress our science has to play an important part, in that by its discoveries it helps the Soviet nation to discover and exploit more fully our national resources. The Party has imposed a definite task on Soviet science: "To develop further progressive Soviet science, which should occupy the leading place in world science. To direct the efforts of scientists toward the more rapid solution of the problems of the utilization of the enormous natural resources of our country. To strengthen the creative collaboration of science and industry, bearing in mind that this collaboration strengthens the experimental basis of science, and at the same time helps the industrial workers to solve their problems more quickly".**

The chemical institutes of the Academy of Sciences, USSR, are developing their work in accordance with the fifth Five-Year Plan. The great majority of the workers of these institutes takes part in solving the more important problems of development of the national economy. It is essential that the work of scientific research institutes should be properly coordinated, both in the Academies of Science and in the educational establishments of the Soviet Union. The concentration of scientific resources on the study of key problems is an essential condition for their better solution.

Parallel with the elucidation of theoretical problems of chemistry, the Institutes of the Division of Chemical Sciences should display more initiative and confidence in the application of the discoveries made by them to national economy. Of the theoretical problems which should above all engage the attention of chemical institutes, that of the theory of chemical structure is one of the most important. Not less important are the theoretical elucidation of the problems of velocity of chemical processes, of the reactivity of compounds, and of the thermodynamics of chemical reactions, and the study of the connection between the physical properties and the chemical structure of natural and synthetic high molecular substances. Much more attention should be given to the study of protein chemistry and of that of biogenic substances.

Modern chemical and physical methods of study should be more and more widely applied to scientific

* Directives of the XIX Party Congress on the Five-Year Plan for the development of the USSR, for 1951-1955. State Political Press, 1952, p. 28.

** G. Malenkov. Report to the XIX Party Congress on the work of the Central Committee VKP (b). State Political Press, 1952, p. 78.

research; this refers particularly to the use of radioactive and stable isotopes as labelled atoms.

Soviet chemists are confronted with the task of collaborating with other scientists in order, by a profound investigation of theoretical problems, to achieve generalizations of a fundamental character. One of the stages of this work should be the publication of monographs on the more important divisions of chemistry.

The Soviet Government and the Party have devoted much attention to the work of scientists. In no country do there exist such favorable conditions for the development of science as have been provided in our country. Suffice it to say that the number of scientific research institutes, laboratories, and other scientific institutions in the USSR has risen, as was reported by G. M. Malenkov at the XIX Party Congress, from 1560 in 1939 to 2900 at the beginning of 1952, and the number of scientific workers has doubled over the same period. During the last Five-Year Plan period the State has spent 47.2 milliard roubles on the development of science.

G. M. Malenkov reported that, as a result of the efforts of the Central Committee of the Party, many domains of science were found to be fostering outlooks and traditions which were alien to Soviet people, and to tolerate the establishment of closed castes of scientists, and to be intolerant of criticism. Various manifestations of bourgeois ideology were revealed and eradicated, as were also all sorts of vulgarizing deviations. "Discussions in the domains of philosophy, biology, physiology, linguistics, and political economy have revealed serious ideological shortcomings in various domains of science, and gave an impulse toward the levelling of criticisms and the conflict of views, and have thus contributed to the development of science. Arakcheyev regimes existing on many sectors of the scientific front have been overthrown. There still persist, however, in a number of branches of science, incompletely liquidated monopolist cliques, which avoid contact with the younger generation of scientists and who fence themselves off from criticism, attempting to settle scientific problems by administrative means. There can be no branch of science which can develop successfully in the stuffy atmosphere of mutual admiration and overlooking of each other's errors: attempts at creation of such cliques of scientists lead inevitably to stagnation and decadence in science".

A number of Soviet scientists have also fallen into grave error regarding the theory of chemical structure. The 1951 discussions of the state of this theory in organic chemistry disclosed certain ideological errors, and indicated the way toward the further fruitful development of A. M. Butlerov's materialistic theory. It is essential that we should continue to strive for such a state of affairs of science in which all the more important problems of theory, in all of the branches of chemistry, are developed according to the progressive ideas based on dialectical materialism.

Soviet chemistry has based its development on the glorious traditions of Lomonosov, Mendeleev, Butlerov, and other Russian scientists. The very numerous cadres of highly qualified Soviet chemists have, by their creative work shown that they are capable of performing the greatest tasks which our Fatherland and the Party may entrust to Soviet chemical science.

Inspired by the resolutions of the XIX Congress of the Communist Party, our chemists will march confidently with the nation towards the triumph of communism, under the leadership of our leader and teacher, the architect of communism, beloved Comrade Stalin.

* G. Malenkov, loc. cit., p. 96.

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ADSORPTION OF GASEOUS MIXTURES

PART 2. ADSORPTION OF ETHYLENE AND PROPYLENE ON ACTIVE CHARCOAL

B. P. Bering and V. V. Serpinsky

1. Introduction

It was shown in Part 1 of this series [1] how important is the systematic study of simultaneous adsorption of mixtures of gases on adsorbents of different structure and nature. These studies are important, first because they contribute to the widening and deepening of current theoretical views on adsorptional phenomena generally, and second because they are necessary (although not always adequate) for the understanding, and the quantitative treatment, of the more important practical applications of adsorptional phenomena, in particular the use of adsorbents for the separation of mixtures. The present paper is devoted to the study of simultaneous adsorption of ethylene and propylene on activated charcoal.

2. Experimental

The same methods and apparatus were used in this study as in that of simultaneous adsorption of ethylene and carbon dioxide [1]. The method depends on mixing known volumes of each of the gases, followed by measurement of the total pressure and the composition of the equilibrium mixture, determined by means of a precision gas analyzer, the action of which is based on the dependence of the thermal conductivity of a gaseous mixture on its composition and pressure.

We shall here describe only certain slight modifications which we have introduced into the apparatus described in Part 1 of this series [1]. Our basic concern was to stabilize the working of the gas analyzer and this was achieved by reducing to -90° the temperature of the electrically heated wire of the analyzer, which was made of platinum, "extra" quality, diameter 30μ . According to the new values of "cold" resistance of the wire and of the new "working" temperature chosen for this wire we varied the constant resistances forming the other three branches of the Wheatstone bridge. In its present form, the gas analyzer possesses not only the required high sensitivity (for $C_2H_4 + C_3H_6$ the analyzer is sensitive to changes in the content of either constituent of the order of 0.05%), but also shows high stability of calibration curves with time.

The next modification introduced into the apparatus consisted of immersing the general air thermostat containing the bulb with the adsorbent with the tubes leading into it in a second thermostat through which water from an ultra-thermostat was allowed to flow. This arrangement permitted us to make measurements of adsorption at different temperatures. Special tests were made to ensure that the gas coming into contact with the adsorbent had enough time to assume the temperature of the water thermostat, at the given rate of circulation of the gas, determined by the design and dimensions of the glass circulatory pump.

Measures were taken to reduce to a minimum any pockets of gas which could escape the general circulation, thus somewhat shortening the time needed for achievement of adsorptional equilibrium.

The same granulated activated charcoal was used as in the previous experiments, and ethylene was prepared and purified by the methods described in detail in Communication 1 [1]. The effectiveness of these methods, and the uniformity of the charcoal used, are very well illustrated by the practical identity of the adsorption isotherms with those presented in Communication 1.

Propylene was prepared by a slightly modified Serderens method [2], by dehydration of isopropanol in presence of fused anhydrous sodium bisulfate, at $120-140^{\circ}$. iso-Propanol was added gradually to the $NaHSO_4$ in

a round-bottomed flask fitted with a reflux condenser, immersed in an oil bath, and the gas was collected in a gasometer, after passing it through wash-bottles containing 10% and 50% aqueous KOH. The gas was passed through a bulb immersed in liquid nitrogen, in order to freeze out the propylene, which was then distilled back into the gas-holder; we collected only the fraction boiling within a range of 1-2°, rejecting the initial and final portions of distillate. This operation was repeated several times, and the final product was passed over fused calcium chloride and phosphorus pentoxide, and collected in a bulb immersed in liquid nitrogen, sealed to the adsorption chamber. After exhaustive evacuation of the reaction space, the propylene was transferred to a storage vessel, passing on the way through a column of previously ignited and degassed active charcoal with silica gel. This last operation was described in detail in Communication 1 of this series.

3. Experimental Results

The methods described were applied to measurement of adsorption of the separate components: ethylene at 7° and 25°, at 0-760 mm, and propylene at 7 and 25°, at 0-300 mm. Adsorption of mixtures of the gases was studied at the same temperatures, over the range of pressures 0-300 mm, for the whole range of compositions of the equilibrium mixtures.

Since there are practically no data to be found in the literature for mixtures of gases, and since such data are necessary for the checking of theoretical concepts relating to adsorption of mixtures, we think it would be useful to present our experimental results in tabular form.

In Tables 1-4, as also in succeeding ones, the subscript "1" relates to the less strongly adsorbed gas, ethylene, and the subscript "2" to the more strongly adsorbed propylene. The pressures p are given in mm, and the magnitude of adsorption a in mm/g.

In studying adsorption of mixtures every series of measurements began with introduction of a known volume of propylene into the system, and after determining the equilibrium a and p , successive portions of ethylene were added, keeping the amount of propylene constant. In Tables 3 and 4 each series of measurements begins with a partial pressure of ethylene $p_1 = 0$.

TABLE 1

Adsorption of ethylene at 7° and 25°

P_1	a_1	P_1	a_1
$t = 7^\circ$			
4.5	0.214	90.6	1.089
10.2	0.349	115.9	1.218
19.7	0.505	147.6	1.359
28.4	0.615	183.7	1.500
38.7	0.721	237.0	1.667
48.8	0.805	290.3	1.813
61.0	0.898	338.3	1.928
68.8	0.957		
$t = 25^\circ$			
4.1	0.093	137.6	0.938
6.2	0.137	161.5	1.017
9.4	0.193	204.6	1.138
12.6	0.228	220.5	1.179
16.1	0.278	268.3	1.292
22.1	0.345	330.2	1.420
36.0	0.460	381.2	1.501
48.0	0.545	494.0	1.686
64.0	0.631	579.4	1.804
75.6	0.687	679.5	1.928
91.0	0.767	771.3	2.030
104.2	0.810		

TABLE 2

Adsorption of propylene at 7° and 25°

P_2	a_2	P_2	a_2
$t = 7^\circ$			
0.2	0.161	80.0	2.422
1.8	0.619	95.0	2.525
7.6	1.149	104.0	2.573
17.5	1.542	138.0	2.732
18.7	1.590	173.7	2.863
25.4	1.751	214.8	2.987
33.9	1.915	220.7	3.005
34.7	1.927	254.5	3.086
46.4	2.092	292.2	3.164
58.0	2.234	333.8	3.240
$t = 25^\circ$			
3.3	0.570	104.1	2.081
7.6	0.802	121.5	2.175
8.3	0.828	139.9	2.260
15.8	1.081	188.6	2.439
25.3	1.296	192.0	2.435
38.0	1.504	237.0	2.585
39.8	1.521	252.5	2.611
54.4	1.703	256.5	2.621
73.5	1.878	280.2	2.679
77.3	1.904	325.5	2.760

4. Discussion of Results

In its general outlines the adsorption of ethylene-propylene mixtures on activated charcoal closely resembles that for ethylene-carbon dioxide mixtures [1]. In representing the experimental results for adsorption of mixtures we plot the equilibrium partial pressures of both gases, p_1 and p_2 , on two axes, and on the third coordinate axis we plot the values a_1 and a_2 for the adsorption of each component, and also the value for summated adsorption $a_{12} = a_1 + a_2$.

For both the temperatures studied (7° and 25°), the adsorption surfaces for ethylene, $a_1 = f_1(p_1, p_2)$, and propylene, $a_2 = f_2(p_1, p_2)$, as well as that for summated adsorption, $a_{12} = f_3(p_1, p_2)$, which we do not represent in this paper in order to save space, have practically the same appearance as do the corresponding surfaces for the system $\text{CO}_2\text{-C}_2\text{H}_4$. Certain differences are apparently due to the closer resemblance of the C_2H_4 molecule to C_2H_6 than to CO_2 , and to the greater difference between adsorption of ethylene and propylene than between ethylene and carbon dioxide.

TABLE 3

Simultaneous adsorption of ethylene and propylene at 7°

P ₁	P ₂	a ₁	a ₂	P ₁	P ₂	a ₁	a ₂
0	17.5	0	1.542	98.0	69.9	0.201	2.223
10.9	17.8	0.052	1.542	123.8	75.2	0.271	2.218
30.4	19.3	0.137	1.541	184.7	83.8	0.373	2.209
82.2	22.9	0.315	1.540	229.3	90.1	0.441	2.203
114.3	25.9	0.426	1.534	0	95.0	0	2.525
176.2	29.1	0.579	1.531	28.5	100.4	0.052	2.520
270.3	36.2	0.777	1.525	67.2	108.8	0.122	2.512
0	33.9	0	1.915	116.6	116.6	0.194	2.504
11.1	35.6	0.040	1.913	173.5	128.3	0.278	2.493
32.1	37.6	0.108	1.911	0	138.0	0	2.732
58.5	40.7	0.185	1.908	29.1	142.2	0.042	2.728
102.8	45.3	0.295	1.904	57.5	150.2	0.090	2.720
151.3	49.6	0.400	1.900	95.5	156.5	0.137	2.714
203.8	56.2	0.506	1.894	157.7	168.7	0.216	2.703
250.3	60.2	0.584	1.890	0	220.7	0	3.005
0	58.0	0	2.234	20.3	224.5	0.024	2.994
14.1	59.4	0.038	2.233	75.2	235.6	0.085	2.983
27.3	61.7	0.072	2.230				

less convex, while with a partial pressure of 50 mm of propylene the isotherm becomes nearly a straight line, i.e., a broadening of the Henry region occurs. The corresponding sections for 7° are of the same nature. We first encountered this straightening effect on the adsorption isotherms of the less strongly adsorbed component when studying the system CO₂-C₂H₄, when we explained it as being due to the heterogeneity of the surface of the charcoal. As will be shown below, this explanation receives further confirmation when considered from the point of view of heats of adsorption of gaseous mixtures.

TABLE 4

Simultaneous adsorption of ethylene and propylene at 25°

P ₁	P ₂	a ₁	a ₂	P ₁	P ₂	a ₁	a ₂
0	7.6	0	0.802	46.9	82.2	0.094	1.870
17.8	8.2	0.092	0.801	87.1	86.0	0.159	1.866
52.0	10.0	0.236	0.800	148.0	93.9	0.254	1.859
115.3	13.7	0.452	0.796	213.6	101.5	0.343	1.852
207.9	17.3	0.686	0.793	0	121.5	0	2.175
269.0	20.2	0.814	0.790	20.1	124.2	0.032	2.172
0	39.8	0	1.521	39.2	127.5	0.061	2.169
17.1	40.8	0.046	1.520	120.3	142.4	0.172	2.155
47.7	43.7	0.121	1.518	169.0	148.6	0.229	2.149
126.3	49.9	0.275	1.516	0	192.0	0	2.435
173.7	54.8	0.371	1.507	35.3	200.0	0.046	2.427
259.0	61.1	0.503	1.502	88.1	210.5	0.106	2.417
0	73.5	0	1.878	0	256.5	0	2.621
17.0	77.2	0.035	1.874	35.7	266.8	0.036	2.612

In our previous paper we introduced, for the characterization of selectivity of adsorption of the more strongly adsorbed component, the so-called selectivity coefficient α_2 , determined by the equation

$$\alpha_2 = \frac{N_2 N_1}{N_1 N_2} = \frac{N_2^0}{N_1^0} \frac{P_1}{P_2} = \frac{a_2}{a_1} \frac{P_1}{P_2} \quad (1)$$

The results obtained for the system C₂H₄-C₃H₆ are in full agreement with the more important qualitative conclusions made on the basis of an analysis of the behavior of the system C₂H₄-CO₂.

Fig. 1 represents sections of the adsorption surface for propylene, $a_2 = f_2(P_1, P_2)$, at 25°, by the planes $P_1 = \text{const.}$, at the partial pressures of ethylene 0, 50, 100, 200, and 250 mm. It is evident that considerable variations in ethylene concentration have little effect on adsorption of propylene, and do not change the shape of the adsorption isotherms. The effect on adsorption of ethylene of varying propylene concentration is quite different, however, as appears from Fig. 2, which represents sections of the adsorption surface for ethylene $a_1 = f_1(P_1, P_2)$ by the planes $P_2 = \text{const.}$, corresponding with the partial pressures of propylene 0, 5, 12.5, 25, 50, 100, 150, and 200 mm. Even quite small concentrations of propylene in the gaseous phase greatly depress adsorption of ethylene, and change the shape of the isotherms of this component. With values of P_2 as low as 5 mm the adsorption isotherm for ethylene becomes far

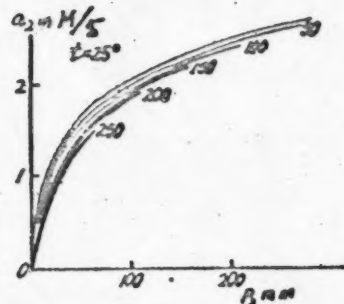


Fig. 1. Sections of the surface $a_2 = f_2(P_1, P_2)$ by the planes $P_1 = \text{const.}$

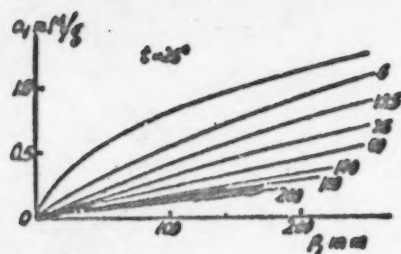


Fig. 2. Sections of the surface $a_1 = f_1(p_1, p_2)$ by the planes $p_2 = \text{const.}$

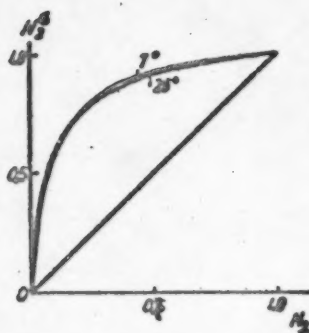


Fig. 3. Relation between molar proportion of propylene in the adsorbed phase N_2^a and its molar proportion in the gaseous phase N_2 at 7° and 25° .

curvature of which gradually diminishes with increase in p_1 . The figures placed at the points of intersection of these curves with the line representing constant total pressure $P = 300$ mm represent adsorption of ethylene in mm/g. A closely similar system of isosteres was obtained at a different temperature (7°).

The isosteres of Fig. 4 served for the construction of the isosteres of total adsorption $a_{12} = a_1 + a_2$, which are represented in Fig. 5, in which the 25° isosteres are shown as broken lines, and the 7° isosteres as continuous lines. The figures placed at the ends of the isosteres represent total adsorption in mm/g.

Over the whole range of pressures studied, the total adsorption isosteres for the system $C_2H_4-C_3H_6$ are, within the limits of experimental accuracy and of the error of interpolation, straight lines for both temperatures, the slope of the lines gradually rising with increase in the degree of filling up of the active surface. This empirical relationship was also found in the previously studied system, $CO_2-C_2H_4$, for which the total adsorption isosteres were also straight lines; from our point of view this is of considerable interest, and has been found to hold for both gaseous mixtures studied by us. Papers on adsorption of mixtures of gases published during the past few years [3-6] are neither detailed enough nor sufficiently accurate to allow us to make use of these data for checking the linearity of total adsorption isosteres.

If this empirical relationship turns out to be a not special case, but to be of more general applicability, at least for the case of low degrees of filling up of the active surface, it would be of importance, inasmuch as it would permit the construction of the total adsorption surface from the adsorption isotherms of the individual

where N_2^a , N_1^a and N_2 , N_1 are the molar proportions of each component in the adsorbed and the gaseous phase, respectively, and p_2 and p_1 are the partial pressures of the components in the gaseous phase. For the system $CO_2-C_2H_4$ the coefficient α_2 for ethylene remains approximately constant at constant total pressure, but diminishes with increase in total pressure. For the system $C_2H_4-C_3H_6$ the selectivity coefficient for propylene is not constant at constant total pressure, and falls slightly with increasing N_2 of propylene in the gaseous phase, and with rising total pressure.

Fig. 3 shows the relation between N_2^a and N_2 of propylene, at a total pressure of 300 mm, at 7° and 25° . It appears from these curves that the coefficient α rises slightly with falling temperature. Thus the value of the selectivity coefficient varies inversely with total pressure and temperature.

For the system $C_2H_4-C_3H_6$ the coefficient α remains approximately constant for the vertical sections of the adsorption surfaces made along the lines of constant summated adsorption, $a_{12} = \text{const.}$, which we shall call sections of constant total filling of the surface; constancy of α is not observed in the sections of the adsorption surfaces by the planes of constant total pressure $P = \text{const.}$ For the system $CO_2-C_2H_4$ the coefficient α remains practically constant for both the sections $P = \text{const.}$ and $a_{12} = \text{const.}$, probably because it does not greatly depend on pressure, and the given sections do not differ as much from each other as do the corresponding ones for the system $C_2H_4-C_3H_6$.

Fig. 4 represents projections of adsorption isosteres of both components $a_1 = \text{const.}$ and $a_2 = \text{const.}$ on the coordinate surface $a_1 = 0$ at 25° . The family of adsorption isosteres for propylene $a_2 = \text{const.}$ approximate fairly close, a family of straight lines. The figures placed near the ends of these lines on the p_2 axis represent adsorption of propylene in mm/g. The family of adsorption isosteres for ethylene is a system of curved lines, the

curvature of which gradually diminishes with increase in p_1 . The figures placed at the points of intersection of these curves with the line representing constant total pressure $P = 300$ mm represent adsorption of ethylene in mm/g. A closely similar system of isosteres was obtained at a different temperature (7°).

The isosteres of Fig. 4 served for the construction of the isosteres of total adsorption $a_{12} = a_1 + a_2$, which are represented in Fig. 5, in which the 25° isosteres are shown as broken lines, and the 7° isosteres as continuous lines. The figures placed at the ends of the isosteres represent total adsorption in mm/g.

Over the whole range of pressures studied, the total adsorption isosteres for the system $C_2H_4-C_3H_6$ are, within the limits of experimental accuracy and of the error of interpolation, straight lines for both temperatures, the slope of the lines gradually rising with increase in the degree of filling up of the active surface. This empirical relationship was also found in the previously studied system, $CO_2-C_2H_4$, for which the total adsorption isosteres were also straight lines; from our point of view this is of considerable interest, and has been found to hold for both gaseous mixtures studied by us. Papers on adsorption of mixtures of gases published during the past few years [3-6] are neither detailed enough nor sufficiently accurate to allow us to make use of these data for checking the linearity of total adsorption isosteres.

If this empirical relationship turns out to be a not special case, but to be of more general applicability, at least for the case of low degrees of filling up of the active surface, it would be of importance, inasmuch as it would permit the construction of the total adsorption surface from the adsorption isotherms of the individual

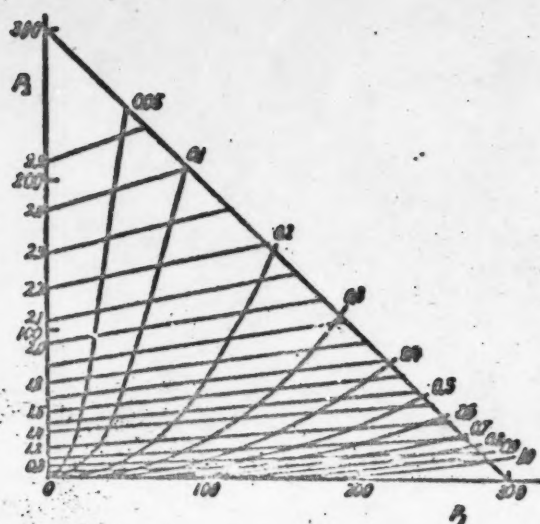


Fig. 4. Family of adsorption isosteres for propylene $a_2 = \text{const.}$ (straight lines) from 0.6 to 2.5 mm/g., and of isosteres for ethylene (curved lines) from 0.05 to 1.0 mm/g. The axes represent partial pressures of ethylene (p_1) and propylene (p_2) in mm.

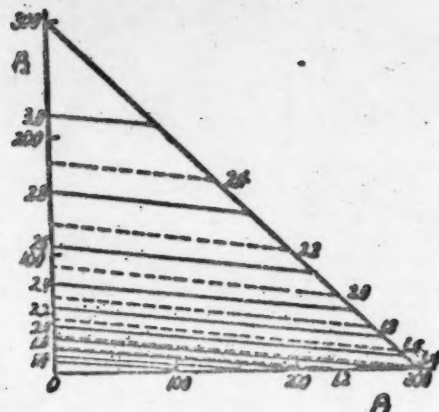


Fig. 5: Family of total adsorption isosteres for ethylene and propylene $a_{12} = a_1 + a_2 = \text{const.}$, from 1.2 to 3.0 mm/g., at 7° (continuous lines), and from 1.2 to 2.4 mm/g., at 25° (broken lines). The coordinates are partial pressures of ethylene (p_1) and propylene (p_2), in mm.

components. If the total adsorption isosteres are straight lines, then the construction, therefrom, of total adsorption surfaces should be very simple. It should be enough to plot on the coordinate planes $p_2 = 0$ and $p_1 = 0$ the adsorption isotherms of the individual components of the mixture $a_1^0 = f_1(p_1, 0)$ and $a_2^0 = f_2(p_2, 0)$, and then to imagine that along these two isotherms, as if along rails, a third straight line, parallel to the coordinate surface $a_1 = 0$, is slid. The surface traced by the movement of this line will be the total adsorption surface.

The constancy of the coefficient α in the sections for constant total degree of saturation of the surface was noted above. It is evident that in every such section the curves $a_1 = f_1(p_1, p_2)$ and $a_2 = f_2(p_1, p_2)$ at $a_{12} = \text{const.}$ will be represented by hyperbolic equations, fully determined by the parameter α . Hence if we could in any way find the nature of the dependence of α on the degree of saturation of the active surface this should, on the condition of the linearity of the total adsorption isosteres, be sufficient for the construction of the surfaces $a_1 = f_1(p_1, p_2)$, $a_2 = f_2(p_1, p_2)$, and $a_{12} = a_1 + a_2$ from the isotherms of adsorption of the individual components. We shall return to this question in the next part of this series.

The following illustrates how closely linear are the total adsorption isosteres for the system $C_2H_4-C_3H_6$. After completing the measurements of adsorption of the mixtures, and the working out of the experimental results, the isosteres of Fig. 5 were produced, to cut the p_1 axis, thus giving a series of extrapolated points on the adsorption isotherm for pure ethylene; the extrapolation was continued up to a pressure of 750 mm. Direct measurements of adsorption of ethylene at 25° and at pressures of up to 760 mm were then made, and the points so obtained were found to lie satisfactorily on the extrapolated curve above.

5. Certain Thermodynamic Considerations

Measurements of simultaneous adsorption of ethylene and propylene were made at two different temperatures, with the object of elucidating the nature of the changes in differential heat of adsorption of each component of the mixture. As is well known, the differential heats of adsorption of a single substance can be derived by the Clausius-Clapeyron equation from the adsorption isosteres, or approximately from two adsorption isotherms at two different temperatures. The differential heats of adsorption of each component were thus calculated, for different values of the degree of saturation of the active surface.

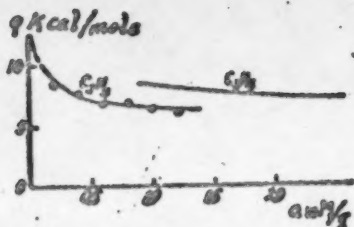


Fig. 6. Differential heats of adsorption of ethylene and propylene, in relation to degree of saturation of the adsorbent surface
1) q kg-cal/mole

Fig. 6 shows the curves relating differential heats of adsorption of ethylene and propylene to magnitude of adsorption. Owing to the steep slope of the initial section of the adsorption isotherms for propylene, the heats calculated for adsorptions less than 1.0 mm/g are not trustworthy. The differential heat of adsorption q of ethylene at first falls steeply, and then more gradually, almost linearly, with increasing saturation of the adsorbent surface.

From the adsorption isotherms for ethylene we calculated the change in free energy, by integrating from the Gibbs' equation, and we then calculated the integral heats of adsorption Q at different degrees of saturation of the surface, by substituting in equations of the type of (2). Graphical differentiation of the curve $Q = Q(a)$ so obtained gave the differ-

tial heats of adsorption $q = \partial Q / \partial a$; the values so obtained are represented by circles on Fig. 6. The good agreement found between the values of q calculated by two methods is evidence of the satisfactory accuracy of the calculation of change in free energy from the adsorption isotherms for ethylene. Similar calculations for propylene are, unfortunately, as little trustworthy as are the calculations of heats of adsorption from two adsorption isotherms.

We are not aware of any published papers dealing with the calculation of differential heats of adsorption of mixtures of gases, for which reason we think that the matter merits a detailed consideration. The integral heat of adsorption of a binary mixture of gases Q_v can obviously be derived from the equation

$$-Q_v = U - F - T \left(\frac{\partial F}{\partial T} \right)_{v, a_1, a_2} \quad (2)$$

in which U is the change in internal energy, F is the change in external energy, and V is the volume of the system.

In order to calculate Q_v from equation (2) it is necessary to find F and $(\partial F / \partial T)_{v, a_1, a_2}$ from Gibbs' equation (3):

$$dF = RT a_1 d \ln p_1 + RT a_2 d \ln p_2 \quad (3)$$

In which we shall, for the sake of simplicity, put pressure instead of fugacity.

Applying to equation (3) the formula for differentiating by parts, in order to change from the independent variables p_1 and p_2 to the independent variables a_1 and a_2 , and integrating the equation so obtained from zero along the path $a_2 = 0$ to some value of a_1 , and then along the path $a_1 = \text{const.}$ to the point (a_1, a_2) , we obtain the change in free surface energy associated with adsorption of a_1 moles of the first and a_2 moles of the second component on an initially free surface. By calculating the partial derivative $(\partial F / \partial T)_{v, a_1, a_2}$ and substituting these values in equation (2) we obtain the following expression for Q_v

$$Q_v = \int_0^{a_1} RT^2 \left[\frac{\partial \ln p_1(a_1, 0)}{\partial T} \right]_{v, a_1, a_2} da_1 + \int_0^{a_2} RT^2 \left[\frac{\partial \ln p_2(a_1, a_2)}{\partial T} \right]_{v, a_1, a_2} da_2 \quad (4)$$

Since the first term of the right-hand side of equation (4) is the integral of the heat of adsorption of the first component along Q_1^0 we can, omitting the subscript v , write the equation in the form

$$Q = Q_1^0 + \int_0^{a_2} RT^2 \left[\frac{\partial \ln p_2(a_1, a_2)}{\partial T} \right]_{a_1, a_2} da_2 \quad (5a)$$

Integrating at first along the path $a_1 = 0$, and then along the path $a_2 = \text{const.}$ to the point (a_1, a_2) we obtain the completely analogous equation

$$Q = Q_2^0 + \int_0^{a_1} RT^2 \left[\frac{\partial \ln p_1(a_1, a_2)}{\partial T} \right]_{v, a_1, a_2} da_1 \quad (5b)$$

where Q_2^0 is the integral heat of adsorption of the second component alone.

Equations (5a) and (5b) serve for derivation of the integral heat evolved during the simultaneous adsorption of a_1 moles of the first, and a_2 moles of the second component of the mixture.

Differentiating equation (5a) with respect to a_2 and equation (5b) with respect to a_1 , we obtain the differential heat of adsorption of each component adsorbed simultaneously:

$$\left. \begin{aligned} q_1 &= \left(\frac{\partial Q}{\partial a_1} \right)_{a_2} = RT^2 \left[\frac{\partial \ln p_1(a_1, a_2)}{\partial T} \right]_{a_1, a_2} \\ q_2 &= \left(\frac{\partial Q}{\partial a_2} \right)_{a_1} = RT^2 \left[\frac{\partial \ln p_2(a_1, a_2)}{\partial T} \right]_{a_1, a_2} \end{aligned} \right\} \quad (6)$$

Representing the differential heat of adsorption of a mixture of the composition (N_1, N_2) by q_{12} , we obtain

$$q_{12} = N_1 q_1 + N_2 q_2. \quad (7)$$

For a mixture of the equilibrium composition $N_1 = p_1/P$, $N_2 = p_2/P$, $P = p_1 + p_2$ etc., whence

$$q_{12} = \frac{p_1}{P} RT^2 \left(\frac{\partial \ln p_1}{\partial T} \right)_{a_1, a_2} + \frac{p_2}{P} RT^2 \left(\frac{\partial \ln p_2}{\partial T} \right)_{a_1, a_2} = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_{a_1, a_2} \quad (8)$$

On the basis of the families of isosteres of adsorption of both components at two different temperatures we calculated, using equation (6) the differential heats of adsorption of ethylene q_1 and propylene q_2 from mixtures of the two gases; the results are represented in Figs. 7 and 8.

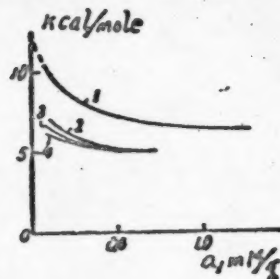


Fig. 7. Differential heats of adsorption of ethylene q_1 depending on adsorption of ethylene a_1 at constant values of a_2 : 1) $a_2 = 0$; 2) $a_2 = 1.0$; 3) $a_2 = 1.4$; 4) $a_2 = 1.6$.

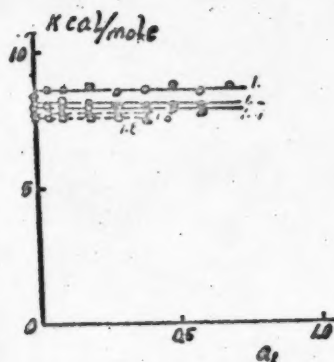


Fig. 8. Relation between differential heats of adsorption of propylene q_2 and adsorption of ethylene a_1 at constant values of a_2 . The figures placed at the ends of the curves relate to adsorption of propylene in mm/g.

Fig. 7 shows the dependence of the differential heat of adsorption of ethylene q_1 on the amount of adsorption a_1 , at various constant values of adsorption of propylene a_2 . It is evident from this graph that the presence of propylene in the adsorbed phase causes considerable diminution in the differential heat of adsorption of ethylene. In other words, the propylene molecules occupy the parts of the surface which have the greatest values for energy of adsorption, and under these conditions the ethylene molecules are in general

adsorbed on those parts of the surface which have lower (and more uniform) values of energy of adsorption than when ethylene alone is adsorbed. From our point of view, this fact is in full agreement with the widening of the Henry region of the adsorption isotherms of ethylene in the presence of propylene.

Fig. 8 shows the relation between differential heats of adsorption of propylene q_2 and the amount of adsorption of ethylene a_1 , at constant values of a_2 . With $a_2 = \text{const}$, the heat of adsorption of propylene is practically independent of the ethylene content of the adsorbed phase, and falls only very gradually with increase in the propylene content. Thus the presence of ethylene does not interfere with adsorption of propylene molecules on the parts of the surface giving higher values of adsorption energy.

It is of considerable interest for the thermodynamic analysis of the properties of the adsorbed phase to know the partial values for change in free surface energy, i.e., the partial two-dimensional pressures. It should be noted that Rowley and Innes have published a series of papers [6] on the thermodynamics of adsorption of

mixtures, dealing in particular with changes in free surface energy associated with this process. Their analysis of these variations seems, however, to be valueless to us, since it is based on a gross thermodynamic error. If we integrate equation (3) we obtain:

$$\Delta F = \pi \sigma = \int_0^{P_1} RT a_1 d \ln p_1 + \int_0^{P_2} RT a_2 d \ln p_2 \quad (9)$$

(here π is two-dimensional pressure, and σ is specific surface of the adsorbent). The sum of the two integrals of the right-hand side of this equation does not, of course, depend on the path of integration, since this sum gives the change in the function of state. It is, however, quite unreasonable to assume, as do Innes and Rowley, that each integral can separately be considered as a change in some function of state, and to call it the partial two-dimensional pressure of the given component. On the contrary, it can readily be shown that, taken separately, these integrals depend on the path of integration. For this reason, the thermodynamic conclusions drawn by Rowley and Innes from this are meaningless.

It might have been possible, having calculated the total two-dimensional pressure from formula (9) to assume, by analogy with the three-dimensional case, that $\pi_1 = N_1^0 \pi$, but with quite considerable deviations from ideality, such as appear to be the rule in the surface layer, such a determination could have only a purely formal value. It would be of considerable interest to determine the partial two-dimensional pressure in an analogous way to that applied by Temkin [7] to grossly non-ideal three-dimensional systems. In that case, however, we would require accurate measurements of adsorption, down to very small degrees of saturation of the active surface, which we have not done. These considerations oblige us, at the present time, to abstain from attempting an analysis of the equations of state of binary adsorption layers.

The authors take this opportunity to express their gratitude to M. M. Dubinin and B. V. Ilyin for their unfailing interest and assistance in the present research.

SUMMARY

1. Simultaneous adsorption of ethylene and propylene on active charcoal has been studied, at 7° and 25°.
2. The adsorption surfaces found greatly resemble those reported in an earlier paper for simultaneous adsorption of carbon dioxide and ethylene on the same sample of active charcoal.
3. Families of adsorption isosteres are constructed for each component separately and for both together, and the projections of the total adsorption isosteres on the plane $a_1 = 0$ are shown to be straight lines.
4. The selectivity coefficient is shown to be constant in the section of constant total saturation of the active surface.
5. Formulas are derived for integral and differential heats of adsorption of the components from mixtures of gases. These formulas are used to calculate the partial differential heats of adsorption.
6. The question of partial two-dimensional pressures in a binary adsorption layer is considered, and a gross thermodynamic error made by Innes and Rowley is pointed out.

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STUDIES OF CAPILLARY CONDENSATION OF VAPORS IN HIGHLY DISPERSE SYSTEMS

PART I. CALCULATION OF CAPILLARY CONDENSATION IN THE VICINITY OF POINTS OF CONTACT OF SPHERICAL PARTICLES

L. V. Radushkevich

The study of capillary condensation of vapors in highly disperse systems is of both theoretical and practical importance, in view of the wide distribution of such systems, and of their frequent practical application. It is generally believed that capillary condensation of vapors takes place in the fine pores of highly disperse substances as a result of the lowering of vapor pressure over the concave meniscus of the liquified substance. Papers have been published [1-3] dealing with this effect, and connected with the verification of the Thomson-Kelvin equation. However, in spite of the numerous studies in this direction, and of discussions of the deviations from the equation found, these papers cannot be considered to be entirely satisfactory. It appears to us that up to now the question has not been clearly enough defined, from the physical point of view. The quantitative description of the process in ordinary porous substances involves a number of arbitrary assumptions regarding the shape of the pores, which is assumed to be simple, although it is generally known that the structure of pores is as a rule complex. In those cases in which the workers dealt with pores of a definite shape, as in the researches of Shereshevsky [2] and Chmutov [3], they avoided the study of the process taking place in porous substances, and did not possess sufficient information regarding the structure of the walls of their artificially formed capillaries and fissures.

Incidentally, the problem of capillary condensation in an artificial fissure formed between a convex lens and a plane surface, which was solved by Chmutov [3], seems to us to be the most promising, inasmuch as it introduces the idea of the process in the vicinity of the point of contact. Continuing this line of thought, we arrive at the concept of condensation of vapors on contiguous bodies, in general, as well as at the special case of condensation in systems consisting of numerous small particles in contact with each other. To such systems would belong various powders, and precipitates of highly disperse substances. In those cases in which the size and shape of the particles are known sufficiently well, and in which measurements of adsorption have shown that capillary condensation pores are absent from the individual particles, the systems are the most suitable for the study of capillary condensation. They are of interest both as models, and for their intrinsic importance, and are particularly suitable for the solution of the problems when the constituent particles have some simple shape.

Certain varieties of soot fulfill these requirements. Electronmicroscope studies of certain soot particles show that they are of spherical form; these findings are beyond doubt, and have been confirmed by numerous authors [4], although no explanation has been advanced as to why they have so simple a shape. Moreover, the size of the particles is quite small, most of them being between 200 and 2000 Å in diameter. A further advantage is that the particles of most specimens of soot have been shown by adsorption measurements not to be porous. Fig. 1* is an electron-photomicrograph of a specimen of lamp-black P-33, prepared by D. G. Kadaner, which shows clearly the spherical shape of the particles. According to Emmett and De Witt and other authors [4] the specific surface of this variety of soot is about 20 m²/g as shown by measurements of adsorption of nitrogen. Its geometrical specific surface, derived from measurements of electron-photomicrographs, is 19.4 m²/g. It may hence be accepted that the individual spherical particles of this material do not in fact possess pores in which additional capillary condensation of vapors could proceed. It is evident from Fig. 1 that the particles are of different sizes, i.e., the system is a polydisperse one. Other varieties of soot are, however, known in which the particle size is practically uniform.*

Capillary condensation of vapors takes place around the numerous points of contact of the particles of compressed pellets of soot; the shape of the crevices between the particles can be known with sufficient accuracy.

* The possibility of capillary condensation in non-porous soots was shown by V. M. Lukyanovich. Spherical particles were also found in aerosols of oxides of metals.

** See page 834.

Each pair of spheres forms a sorption cell, or condensation center, in which appearance of the first portions of liquified vapor leads, on condition of wetting of the surface, to formation of a concave meniscus, and this leads to the development of the process of capillary condensation.

1. General description of the problem

The simple shape of the particles and of the crevices formed between them permit an exact consideration of the process of condensation, without involving any doubtful assumptions regarding the shape of the pores. We can thus, for a sorption cell consisting of spherical particles, undertake to a certain extent "classical" derivation of the capillary condensation isotherms from the Thomson-Kelvin equation. Experimental evidence of the absence of pores in the individual particles render such calculations fully justifiable.

The research consisted of the following. We first calculate capillary condensation for an elementary sorption cell, consisting of two spheres in contact, taking into account measurements of vapor pressure and of corresponding changes in the curvature of the surface of the meniscus. The transition from the elementary cell to a monodisperse system is then made; this system consists of a large number of spheres in contact with each other, and it may be assumed in the simplest case that they are packed in an orderly manner. The full calculation of the capillary condensation isotherm is possible for such a system. This simple model may serve for the discovery of certain general features of the process of condensation of vapors in systems formed of small contiguous particles, and a number of useful generalizations applying to more complex systems of this sort may be made.

The relation between the curvature of the surface and the vapor pressure of a liquid is given by the classical Thomson-Kelvin equation. We initially applied this relation without taking into account deviations from the equation sometime observed during experiments. We believe that with a fully developed condensation process all the deviations can be ascribed only to imperfect knowledge of the surface tension and the molar volume of the liquids. We do not, for this reason, study the process at low relative pressures p/p_s , at which the deviations may assume large proportions, but we confine our analysis of the process to saturations roughly from $p/p_s = 0.5$ to full saturation ($p/p_s = 1$).

The very small radius of the spheres of which our highly disperse systems are made up is very characteristic of them. A consequence of this feature is that we must, in general, in calculating the curvature of the annular meniscus formed around the point of contact of the two spheres of the adsorption cells, take into account the double curvature of the surface, since in the given case both radii of curvature are very small at any point in the meniscus, and are of the same order of magnitude. Under conditions of full wetting the Thomson equation takes the following form, for an adsorption cell:

$$1/p + 1/p^* = \frac{R_s T \ln p_s/p}{\sigma V} = \frac{2}{C} \quad (1)$$

where p and p^* are the radii of curvature of the surface of the meniscus, σ is the surface tension of the liquid, V is the molar volume, R_s is Clapeyron's constant, and T is absolute temperature.

The constant C in equation (1), expressed by the relation

$$C = \frac{2\sigma V}{R_s T \ln p_s/p} \quad (2)$$

has a simple physical sense: it is the radius of curvature of the annular meniscus of the liquid, equivalent to the given capillary cell.

We shall in the future assume full wetting, although there would be no particular difficulty in calculating the angle of contact. Since capillary condensation on spherical particles is always preceded (at low relative pressures) by formation of a monomolecular adsorption layer covering the whole surface, the assumption of full wetting corresponds more closely to reality.

2. Capillary condensation in a sorption cell, for the limiting case.

The volume of condensed liquid around the point of contact of two spheres of equal radius can readily be calculated for the limiting case of full saturation, i.e. when the relative vapour pressure p/p_s is equal to unity. The condition $p/p_s = 1$ leads to a value of $C = \infty$ in the preceding formulas, and in this case the Thomson equation assumes the simple form:

$$1/p + 1/p^* = 0. \quad (3)$$

It hence follows that the meniscus of the liquid around the point of contact of the spheres corresponds to a surface of rotation of zero curvature. It is well known that such a surface is a catenoid, obtained by the rotation of a section of a catenary curve around some axis.

The point of intersection of the coordinates is given by the point of contact of the spheres (Fig. 2), taking as the x axis a line joining the centers of the spheres, and as the y axis a line perpendicular to this. In these circumstances the equation of the catenary curve NM is:

$$y = a \operatorname{ch} x/a.$$

In order to find the volume of condensed liquid it is necessary to determine the parameter a of this curve, as well as the coordinates x_M and y_M of one of the points of contact of the catenary with a sphere (point M). It follows from the condition $\theta = \infty$ that the values of a , x_M , and y_M depend only on the radius of the sphere, R , and not on any material constant.

The equation for a segment, the center of which is on the x axis, and which touches the y axis at its origin, has the form:

$$y = \pm \sqrt{2Rx - x^2}.$$

If the condition of full wetting is accepted, then it is obvious that the catenary must contact the sphere at the point M, on the conditions that

$$\left. \begin{aligned} a \operatorname{ch} x_M/a &= \sqrt{2Rx_M - x_M^2} \\ \operatorname{sh} x_M/a &= \frac{R - x_M}{a \operatorname{ch} x_M/a} \end{aligned} \right\} \quad (4)$$

If for convenience we write $z_0 = R/a$ and $z = x_M/a$, equation (4) takes the form

$$\operatorname{ch} z = \sqrt{2zz_0 - z^2} \quad (5)$$

and

$$\operatorname{sh} 2z = 2(z_0 - z). \quad (6)$$

The second of these gives

$$z_0 = z + \frac{1}{2} \operatorname{sh} 2z. \quad (7)$$

Eliminating z_0 from formulas (5) and (7) we obtain the transcendental equation for the unknown z :

$$\operatorname{sh} 2z = \frac{\operatorname{ch}^2 z}{z} - z, \quad (8)$$

which has one real root, and may readily be solved graphically. We thus find that $z = 0.639$, after which equation (7) gives $z_0 = 1.468$. The value of the parameter a of the catenary can hence readily be calculated, as well as the coordinates of the point M:

$$a = \frac{R}{1.468} = 0.681 \cdot R; \quad x_M = 0.681 \cdot 0.639R = 0.436R; \quad y_M = 0.826R.$$

As was expected, all three characteristics of the geometric conditions for formation of the meniscus are proportional to the radius R . The volume V of the liquid between the two contiguous spheres is obviously equal to that of the catenoid NMN'M' (Fig. 2), less twice the volume of the included segment of the sphere, i.e., $V = V_K - 2w$.

The volume V of the catenoid is given by

$$V_K = \frac{1}{2} \pi a^3 \left(\operatorname{sh} \frac{2x_M}{a} + \frac{2x_M}{a} \right). \quad (9)$$

The values of a and x_M were derived by us above, as fractions of the radius of the spheres, whence it

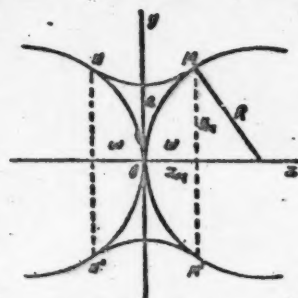


Fig. 2

follows that $2x_M/a = 1.279$, and that $V_K = \frac{1}{2}\pi (0.681)^3 \cdot R^3 (\text{sh } 1.279 + 1.279)$ or $V_K = 0.4640\pi R^3$.

The volume w of the segment of the sphere, height x_M and half-chord length y_M is given by $w = \frac{1}{6}\pi x_M(3y_M^2 + x_M^2)$. Substituting the values of x_M and y_M found by us we obtain $2w = 0.3244\pi R^3$. The volume of liquid formed around the point of contact is thus finally given by $v = V_K - 2w = \pi R^3(0.4640 - 0.3244)$, or

$$v = \frac{1}{3}\pi R^3 \cdot 0.2096 \quad (10)$$

It hence follows that v is proportional to the volume of the contiguous spheres, the coefficient of proportionality being independent of the properties of the liquid or vapor.

We would add that the value of the volume obtained above corresponds with limiting filling of the sorption cell formed by two contiguous spheres. The total amount of capillary-condensed liquid per unit mass of sorbent will be calculated below.

3. Shape and parameters of the meniscus of the liquid obtained by capillary condensation of vapor in a sorption cell (general case).

The above case of limiting filling of a sorption cell formed of two contiguous spheres is that obtained at completion of the process of capillary condensation of vapor in crevices. We were able to show that this state is associated with formation of a concave liquid meniscus of definite shape and dimensions which are independent of the nature of the adsorbate (of its physical constants). The effect of the nature of the vapor undergoing condensation is manifested in the process of filling up of the cells. It is not yet possible to follow the development of the process of condensation with time, i.e., the kinetics of capillary condensation. We cannot for this reason describe the process of appearance of the first portions of liquid around the point of contact, but in general it may be supposed that the process of increase in the amount of condensed vapor, as the equilibrium pressures rise from small to high values, can be represented as a progressive shift of the concave equilibrium meniscus farther and farther from the point of contact. To each relative pressure p/p_s will correspond a given liquid meniscus and a definite volume of liquid in the cell. At the limit, when $p/p_s = 1$, the amount of liquid in the cell will be at a maximum.

We shall now determine the shape of the meniscus and its parameters for the case $p/p_s < 1$, in order to ascertain how the amount of capillary condensed liquid in a cell gradually rises with increasing p/p_s , and thence to construct isotherms of capillary condensation. Under these conditions the magnitude C is finite ($C > 0$), and the problem reduces itself, in the first place, to an analysis of an equation of the type:

$$1/p + 1/p' = \frac{2}{C}. \quad (11)$$

For $p/p_s = \text{const}$, the equation corresponds to the surfaces of a constant final curvature. It is known [5] that one such surface is the so-called nodeid, obtained by the rotation of a flat spiral line (trochoid) around some axis. A second surface with a constant curvature is the unduloid, given by the rotation of an undulating line around a specific axis.

The problem of finding the shape and the parameters of the meniscus of the liquid between contiguous spheres can be solved, in its most general form, one of the solutions corresponding to a concave meniscus, and another to a convex meniscus. It is evident that the second case is connected with the theoretical description of the process of evaporation.

The equation for the meridional curve of the figure of rotation forming the meniscus of the liquid can be derived in the following way. Let AB (Fig. 3) be an arc of the meridional curve, the axis of rotation of which coincides with the line zz' . We shall adopt the arbitrary convention that the direction on the axis z from below up is a positive one, and the abscissas axis u will be drawn through the point of contact of the spheres. c and c' are the centers of curvature of the surface, corresponding with the radii of curvature p and p' at any point of this surface of rotation. It is evident from the figure that

$$\frac{1}{p} = \frac{\sin \tau}{r} \quad \text{and} \quad \frac{1}{p'} = \frac{p}{(1+p')^2 V_s}.$$

where $p = dz/dr$.

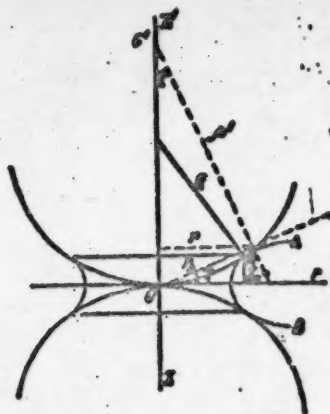


Fig. 3

It is also obvious that $\frac{d}{dr} \sin \tau = \frac{d}{dr} \frac{p}{\sqrt{1+p^2}} =$

$\frac{p'}{(1+p^2)^{3/2}} = \frac{1}{\rho}$. The left-hand side of equation (11) can thus be written in the form

$$\frac{1}{\rho} + \frac{1}{\rho^2} = \frac{d}{dr} \sin \tau + \frac{\sin \tau}{r}$$

or

$$\frac{1}{\rho} + \frac{1}{\rho^2} = \frac{1}{r} \frac{d(r \sin \tau)}{dr}$$

Consequently

$$\frac{1}{r} \frac{d(r \sin \tau)}{dr} = \frac{2}{C} \quad (12)$$

in which $C > 0$.

Equation (12) is the basic differential equation for the derivation of the shape of the meridional curve. The first integration gives:

$$r \sin \tau = \frac{r^2}{C} + \text{const.} \quad (13)$$

In considering how to find the value of the integration constant it should be noted that for all the diverse cases of the meniscus of the liquid between two contiguous spheres the angle τ of slope of the tangent to the oz axis may assume any values, since otherwise an additional condition, devoid of any physical meaning, in the given case, would have to be imposed on formation of the meniscus. We know that of the two meridional curves giving surfaces of constant curvature the undulant curve corresponding to an unduloid has inflection points with finite values of τ , and does not have any points at which $\tau = 2\pi n$. On the other hand, a trochoid has no points of inflection, and for it τ can have any values. These considerations show that in the given case a trochoidal meniscus is formed (in the general case it is convex or concave).

Analysis of equation (13) shows that the variable r varies between the minimum and maximum values. In fact, $\sin \tau$ varies between the limits -1 to $+1$. For these cases we have

$$-r_1 = \frac{r_1^2}{C} + \text{const.} \quad (14)$$

and

$$+r_2 = \frac{r_2^2}{C} + \text{const.} \quad (15)$$

where r_1 and r_2 are the minimum and maximum distances of the trochoid from the zz' axis. It follows from these equations that

$$r_2 - r_1 = C. \quad (16)$$

It is further clear that the value of the angle $\tau = (2n+1)\pi/2$ corresponds to that of a concave meniscus, the examination of which is our object. For this meniscus on the oz axis a distance of the trochoid from zz' of $r = r_1$ is the minimum one. At $\tau = 2n\pi/2$ the value of r achieves a maximum value of r_2 , which corresponds to a convex meniscus. The trochoid is thus characterized by two parameters r_1 and r_2 , which are connected with C as in equation (16). Since in our problem C is known, we need determine only the parameter r_2 .

Substituting the value of the integration constant from equation (14) into equation (13) we obtain

$$\sin \tau = 1/C \left(r - \frac{r_1^2}{r} \right) - \frac{r_1}{r} = \frac{p^2}{\sqrt{1+p^2}}.$$

Solving this equation for $p = dz/dr$ we obtain

$$\frac{dz}{dr} = \pm \frac{r_1 r_2 - r^2}{\sqrt{(r^2 - r_1^2)(r_2^2 - r^2)}} \quad (17)$$

where the upper sign corresponds to the positive direction taken by us on the z axis. It should be noted that in our problem $r_1 r_2$ is always $> r^2$, since the values of r which concern us are close to r_1 .

We obtain from equation (17), on the condition that $z = 0$ for $r = r_2$:

$$z = \pm \int_{r_2}^r \frac{r_1^2 - r^2}{\sqrt{(r^2 - r_1^2)(r_2^2 - r^2)}} dr. \quad (18)$$

The integral of this expression is converted in the usual way into elliptic integrals of the 1st and 2nd orders. Writing for convenience

$$\Delta \phi = \sqrt{1 - K^2 \sin^2 \phi} \quad (19)$$

and assuming that

$$r = r_2 \cdot \Delta \phi, \quad (19')$$

where K is a modulus, and ϕ is the argument of the elliptic integrals. We know that

$$K = \sin \alpha = \sqrt{\frac{r_1^2 - r_2^2}{r_1^2}}. \quad (19'')$$

We then obtain, after substitution of the variables in formula (18):

$$z = \pm [r_1 \phi(\alpha, \phi) - r_2 \psi(\alpha, \phi)]. \quad (20)$$

We have here, for the sake of shortness, assumed

$$\left. \begin{aligned} \phi(\alpha, \phi) &= F(\alpha) - F(\alpha, \phi) \\ \psi(\alpha, \phi) &= E(\alpha) - E(\alpha, \phi) \end{aligned} \right\} \quad (20')$$

where $F(\alpha)$ and $E(\alpha)$ are full elliptic integrals of the 1st and 2nd orders, in the Lefrange form:

$$\left. \begin{aligned} F(\alpha) &= \int_0^{\pi/2} \frac{d\phi}{\Delta \phi} \\ E(\alpha) &= \int_0^{\pi/2} \Delta \phi \cdot d\phi \end{aligned} \right\} \quad (21)$$

The functions $F(\alpha, \phi)$ and $E(\alpha, \phi)$ are elliptic integrals of the first and second orders, from the argument ϕ :

$$\left. \begin{aligned} F(\alpha, \phi) &= \int_0^{\phi} \frac{d\phi}{\Delta \phi} \\ E(\alpha, \phi) &= \int_0^{\phi} \Delta \phi d\phi \end{aligned} \right\} \quad (22)$$

Formula (20) is the equation for the required meridional curve, which is an infinite flat spiral line (trochoid), with the parameters r_1 and r_2 . We are concerned with only a small section of the trochoid near the point with the abscissa r_1 , to which corresponds the concave meniscus of the liquid. The integrals (21) and (22) are tabulated [6]. We have prepared auxiliary tables for the differential integrals ϕ and ψ , entering into formula (20).

The problem of finding the parameters of the trochoid meniscus may be formulated as follows: to make a section of the trochoid for a given value of C , symmetrically in contact with two contiguous circles of radius R . The point of contact of the circles is at the point of intersection of the coordinate axes (Fig. 1), and the centers of the circles are on the z axis. As a result of the symmetry of the system around the r axis the problem may be simplified, and reduced to the derivation of the parameters of a trochoid touching one of the circles, the point of a trochoid with the abscissa r_1 lying on the r axis. We let this contact take place at the point M_1 having the coordinates r_0 and z_0 . The equation for the circumference will have the form

$$z = R \pm \sqrt{R^2 - r^2}.$$

We have for the point of contact M_1 under conditions of full wetting:

$$R - \sqrt{R^2 - r_0^2} = r_1 \phi(\alpha, \phi_0) - r_2 \psi(\alpha, \phi_0) \quad (23)$$

$$\frac{r_0}{\sqrt{R^2 - r_0^2}} = \frac{r_1 r_2 - r_0^2}{\sqrt{(r_1^2 - r_0^2)(r_2^2 - r_0^2)}} \quad (24)$$

In addition, we have the relation

$$C = r_2 - r_1 \quad (25)$$

In the system of equations (23), (24), and (25) the values of r_1 , r_2 , and r_0 are unknown. Obviously $r_2 > r_0 > r_1$.

From equation (24) we find

$$r_0 = \sqrt{\frac{R r_1 r_2}{R + C}} \quad (26)$$

We introduce the non-dimensional magnitudes

$$B = C/R; \quad x = r_1/R; \quad x + B = r_2/R; \quad x_0 = r_0/R$$

Formula (26) then takes the form

$$x_0 = \sqrt{x \frac{x+B}{1+B}} \quad (26^I)$$

After substituting the new values and the value of x_0 in formula (23) we obtain

$$1 - \sqrt{1 - x \frac{x+B}{1+B}} = x [\phi(\alpha, \phi_0) - \psi(\alpha, \phi_0)] - B \psi(\alpha, \phi_0) \quad (27)$$

It follows from equations (19), (19^I), and (19^{II}) that

$$\sin \alpha = \sqrt{1 - \left(\frac{x}{x+B}\right)^2} \quad (28)$$

$$\sin \phi_0 = \frac{1}{\sin \alpha} \sqrt{1 - \frac{\cos \alpha}{1+B}} \quad (29)$$

Equation (27) is solved graphically, at the given value of B . Its right-hand side is a function of x only, since the angles α and ϕ_0 depend on x , according to equations (28) and (29). The graphical construction shows that for each value of B equation (27) has only one root, i.e., x is determined unambiguously.

We shall here outline the solution in principle only. In practice, since the published tables give values of elliptic integrals at different moduli at 5° intervals, and for arguments at 1° intervals, we applied this method, in order to avoid laborious interpolations.

It follows from (28) that $x = B \cdot \eta$, where $\eta = \frac{\cos \alpha}{1 - \cos \alpha}$; the left-hand side of equation (27) then assumes the form:

$$P_1(\eta) = 1 - \sqrt{1 - B^2 \frac{\eta(\eta+1)}{1+B}} \quad (27^I)$$

and the right-hand side will be:

$$P_2(\eta) = B \{ \eta [\phi(\alpha, \phi_0) - \psi(\alpha, \phi_0)] - \psi(\alpha, \phi_0) \} \quad (27^{II})$$

Using the tables, we construct a family of curves for $\psi(\alpha, \phi_0)$ and $\phi(\alpha, \phi_0) - \psi(\alpha, \phi_0)$ in relation to ϕ_0 at values of α through 5° to 85°. All values of η were calculated for each given B , as well as the corresponding values of the angle ϕ_0 from the formula (29). We then used formulas (27^I) and (27^{II}) for the calculation of the functions $P_1(\eta)$ and $P_2(\eta)$, and graphs were drawn, in which the values of the roots η at different B were given by the points of intersection. The unknowns x were finally derived from the relation $x = B\eta$.

We thus found the values of x and $x + B$ for a series of values of the parameter, and we then derived the values of x_0 from formula (26^I), i.e., we achieved a full solution of the problems of the parameters of the meridional curve, which is the concave meniscus of the liquid between two contiguous spheres. The results of these calculations are given in Table 1.

TABLE 1

$\beta = C/R$	$x = r_1/R$	$x_0 = r_0/R$	$x + \beta = r_2/R$
0.05	0.194	0.212	0.244
0.10	0.250	0.282	0.350
0.20	0.325	0.377	0.525
0.30	0.370	0.437	0.670
0.40	0.404	0.482	0.804
0.50	0.432	0.518	0.932
0.60	0.455	0.548	1.055
0.80	0.485	0.588	1.285
1.00	0.502	0.614	1.502
1.50	0.525	0.652	2.025

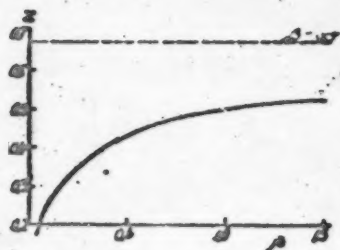


Fig. 4

Increase in the coefficient β is associated with rise in relative vapor pressure p/p_s . The magnitude x represents the relative distance of the middle of the meniscus from the point of contact of the spheres. The values given in Table 1 hence indicate how the meniscus moves in accordance with increase in vapor pressure. Fig. 4 shows the relation between x and β , according to the values of Table 1, and also gives the limiting position of the meniscus, corresponding to the broken line for $p/p_s = 1$, derived as above. We see that for small β (small p/p_s) the distance x between the middle of the meniscus and the point of contact of the spheres rises rapidly, and that the rate of increase is strongly retarded as p/p_s approaches unity. The relationship found is independent of the size of the spheres and of physical constants, i.e., the curve of Fig. 4 is a universal one.

4. Volume of condensed liquid in a sorption cell, for the general case.

The volume of condensed liquid in sorption cells for different values of β or p/p_s can be calculated from the values of the parameters of the meridional curve found above. It is obvious that this volume may be represented as the difference between two volumes:

$$v = V_N - 2w.$$

The first of these, V_N is the volume of the figure of rotation (nodoid) given by rotation of an arc of a trochoid around the x axis, limited by planes of origin parallel to the r axis. The second volume $2w$ is that of segments of the spheres, tangential to the nodoid.

The volume V_N is derived as the volume of a figure of rotation, using formula (17):

$$V_N = 2\pi \int_0^{z_0} r^2 dz = 2\pi \int_{r_1}^{r_0} \frac{r_1 r_2 r^2 - r^4}{\sqrt{(r_2^2 - r^2)(r^2 - r_1^2)}} dr. \quad (30)$$

Here r_0 and z_0 are the coordinates of the point of contact. Introducing the previous symbols from (19), (19'), and (19''), we substitute for the variable in formula (30), to obtain:

$$V_N = 2\pi r_2^2 \int_0^{\pi/2} [r_1^2 \Delta \phi - r_2^2 (\Delta \phi)^2] d\phi$$

or

$$V_N = 2\pi r_2^2 \int_0^{\pi/2} \Delta \phi d\phi - 2\pi r_2^2 \int_0^{\pi/2} (\Delta \phi)^2 d\phi. \quad (31)$$

The first of these integrals is an elliptic integral of the first order, and the second may be reduced to a combination of elliptic integrals. It can be shown that [7]

$$\int_0^{\phi} (\Delta \phi)^2 d\phi = \frac{1}{2} \left(\frac{r_1^2 + r_2^2}{r_2^2} \right) \int_0^{\phi} \Delta \phi d\phi - \frac{1}{2} \frac{r_1^2}{r_2^2} \int_0^{\phi} \frac{d\phi}{\Delta \phi} + \frac{r_2^2 - r_1^2}{6r_2^2} \sin 2\phi \cdot \Delta \phi. \quad (32)$$

Substituting the expression (32) into formula (31), and taking into account the integration limits, we obtain:

$$V_N = \frac{1}{2} \pi \{ r_1^2 \Phi(\alpha, \phi) + \frac{1}{2} r_2 (r_1^2 - r_2^2) \sin 2\phi - [2(r_2 - r_1)^2 + r_1^2] r_2 \Psi(\alpha, \phi) \} \quad (33)$$

Here $\Phi(\alpha, \phi)$ and $\Psi(\alpha, \phi)$ are differential elliptic integrals for the argument ϕ , in accordance with formulation (20).

The doubled volume $2w$ of the spherical segment is given by

$$2w = \frac{1}{2} \pi z_0^2 (3r_0^2 + z_0^2). \quad (34)$$

The previous non-dimensional parameters x , β , and x_0 are introduced into formulas (33) and (34), when the volume v of condensed vapor can be represented as

$$v = \frac{1}{2} \pi R^3 \cdot U, \quad (35)$$

where the non-dimensional function U has the form

$$U = (2 + x_0^2) \sqrt{1 - x_0^2} + x^2 (x + \beta) \cdot \Phi(\alpha, \phi) + \frac{1}{2} x_0 \beta (\beta + 2x) \sin 2\phi - [2\beta^2 + x(x + \beta)] (x + \beta) \Psi(\alpha, \phi) - 2. \quad (36)$$

TABLE 2

β	U	β	U
0.05	$1.43 \cdot 10^{-3}$	0.50	$32.49 \cdot 10^{-3}$
0.10	$3.44 \cdot 10^{-3}$	0.60	$39.45 \cdot 10^{-3}$
0.20	$9.90 \cdot 10^{-3}$	0.80	$53.84 \cdot 10^{-3}$
0.30	$17.45 \cdot 10^{-3}$	1.00	$70.66 \cdot 10^{-3}$
0.40	$24.67 \cdot 10^{-3}$	∞	$209.4 \cdot 10^{-3}$

The values of the parameters x and x_0 , entering into expression (36), are found for different given values of β by the method described above. The corresponding values of α and ϕ_0 are derived from formulas (28) and (29). The integrals Φ and Ψ are found from the tables. For a given radius R of the sphere the relation (36) expresses the relative change in the volume of condensed vapor with change in β , i.e., with change in vapor pressure. Table 2 gives the calculating values of U for certain β , derived by means of formula (36). The values of U for various intermediate β are found from the graph drawn on the basis of the values of Table 2, not shown in this paper.

The last column of the Table gives the value of U for full saturation (when $p/p_s = 1$), derived by us above from the volume of the catenoid (formula 10) for the limiting case. The relative volume U is a universal function of β , independent of the radius of the sphere, and of physical constants. If we introduce the relative vapor pressure p/p_s , and express U as a function of this variable, it becomes evident that the value of U rises as that of R falls. Formula (35) allows us to calculate the volume v of condensed vapor at different p/p_s , and for spheres of different radii.

As an example, we have calculated U and v for spheres of different radii, for capillary condensation of benzene at 20°; the following constants were taken: $\sigma = 28.9$ ergs/sq. cm.; $d_{20} = 0.879$ g/cm³; $M = 78.11$.

Since $C = \frac{2\sigma V}{2.3 R_0 T} \cdot (\log p_s/p)^{-1}$, we obtain the following, after substituting the values of the physical constants:

$$C = 0.917 \cdot 10^{-7} \cdot (\log p_s/p)^{-1}.$$

TABLE 3

p/p_s	$R = 1 \cdot 10^{-6}$ cm		$R = 5 \cdot 10^{-6}$ cm		$R = 1 \cdot 10^{-5}$ cm		$R = 5 \cdot 10^{-5}$ cm	
	$U\%$	$v \cdot 10^{-4}$ m μ^3	$U\%$	$v \cdot 10^{-4}$ m μ^3	$U\%$	$v \cdot 10^{-4}$ m μ^3	$U\%$	$v \cdot 10^{-4}$ m μ^3
0.50	1.77	0.371	0.16	4.2	0.07	14.7	0.01	262
0.60	2.58	0.541	0.26	6.8	0.10	21.0	0.015	393
0.80	6.57	1.377	0.92	24.1	0.32	67.0	0.04	1049
0.90	12.4	2.60	2.48	65	0.99	207	0.095	2490
0.95	16.7	3.50	5.57	146	2.57	540	0.26	6820
1.00	20.9	4.39	20.9	550	20.9	4390	20.9	$55 \cdot 10^4$

Table 3 gives the values of U and v for spheres of different radii, and for certain relative pressures p/p_s . The values of $\beta = C/R$ are calculated using the above value for the parameter C .

The results given in the Table point to certain features of the sorption system under consideration, due to its geometrical properties. The magnitude U is, as is evident from formula (35), a quarter of the relative

volume of capillary-condensed liquid, i.e., it shows what fraction of the volume of the sorption cell is occupied by the liquid in it. It is evident from the data of Table 3 that this fraction is in general a small one, not exceeding about 5% at its limiting value. It is further evident that it falls steeply as the radius of the sphere increases. On the other hand, the volume of sorbed liquid rises steeply as the size of the spheres increases. Finally, the calculation shows that with increase in vapor pressure the volume v rises, at first gradually, and then quite steeply, especially for large particles.

When we proceed to the analysis of the process in systems formed of large numbers of spheres we shall see how these properties of sorption cells affect the total magnitude of sorption, and what effect they have on the form of the capillary condensation isotherms.

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SUMMARY

1. A theoretical analysis of the process of capillary condensation in a system consisting of two contiguous spherical particles of the same radius has been conducted.
2. An expression has been found for the meniscus of the liquid in a sorption cell, on the assumption of full wetting, and the volume of sorbed vapor has been calculated as a function of the vapor pressure.
3. The behavior of a sorption cell has been shown to follow from its geometrical properties.

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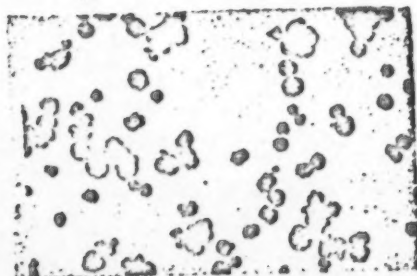


Fig. 1.

CATALYTIC OXIDATION OF PHOSPHINE OVER A WIDE RANGE OF TEMPERATURES

E. A. Andre'y and N. N. Kavtaradze

INTRODUCTION

We have in our earlier papers [1,2] given a detailed description of the results of research on the catalytic oxidation of phosphine at moderate temperatures (18-120°), in presence of charcoal activated with copper salts. We found that, together with a rapid process of physical adsorption, a specific irreversible process of adsorption of phosphine by copper oxides took place. The kinetics of the combined (physical and irreversible) adsorption of phosphine is expressed by a parabolic equation [3]

$$q = At^{1/n},$$

where q is the amount of adsorbed gas, A is a constant, t is time, and $1/n$ is an index of the degree.

We showed that the catalytic oxidation of phosphine on charcoal treated with copper salts involves a stage of chemisorption on copper oxide on charcoal. The kinetics of oxidation of phosphine in the adsorption layer may, over the range 18-120°, be represented by the Roginsky-Zeldovich equation [4]:

$$\log(t + t_0) = \frac{\alpha}{1.3} q - \log(\alpha a),$$

where a is the initial velocity, α is a constant, q is the amount of adsorbed gas, $t = 1/\alpha a$, and t is time in minutes. We thought it would be of interest to investigate this same reaction at higher temperatures.

Before proceeding to describe the results of our studies of the catalytic oxidation of phosphine over the range 264-320°, we shall briefly review published views on the state of the surface of active charcoal. Such a surface, in contact with damp air, adsorbs molecules of water, carbon dioxide, and oxygen. Shilov and Chmutov [5] suppose that in addition to physically adsorbed molecules of oxygen there may exist, under different conditions, three surface oxides, having different ratios of carbon to oxygen.

At 320°, and in a vacuum given by a mercury-diffusional pump, we achieve not only total elimination of physically adsorbed oxygen, but also partial desorption of the oxygen chemically bound by the surface of the charcoal as oxides of carbon. Chemisorbed oxygen is tenaciously retained by the surface of active charcoal, since the heat of adsorption of oxygen at low saturations is close to that of formation of oxides of carbon [6,7]. Complete removal of chemisorbed oxygen from the surface of active charcoal is not achieved even at 900°, with prolonged evacuation.

EXPERIMENTAL

Experimental methods, and preparation of samples of charcoal with chemisorptive and catalytic properties

The apparatus described in our preceding paper, with quartz spring balance, was used for the study of catalytic oxidation of phosphine at 200-320°. The accuracy of the measurements was in most cases within 0.1% by weight, and the temperatures varied by $\pm 0.5^\circ$. The experiments on adsorption and desorption were conducted according to the methods described in our earlier paper [2]. As in our previous researches, we used as the carrier for the catalytic additives ground recuperational carbon AP, with a grain diameter of 1.5 to 2.5 mm., and an ash content of 8%. The specific surface of this charcoal, as determined by the methylene blue method, amount to 410 sq.m/g.

The processes of adsorption and desorption of methanol were studied, in order to obtain a fuller picture of the behavior of the recuperational carbon as an adsorbent.



Fig. 1. 1) Adsorption isotherm, 2) desorption isotherm for methanol, at 20°, for recuperational carbon, subjected to preliminary training in high vacuum at 400°.

Fig. 1 is based on measurements made in A. V. Kiselev's laboratory, and shows the adsorption (1) and desorption (2) isotherms for methanol at 20°, on recuperational carbon previously trained at 400° in high vacuum. The radii of the capillaries were calculated from the Thomson formula, for the desorption branch of the isotherm

$$r = \frac{2\sigma V \cos \theta}{RT 2.3 \log P_2/P}$$

In this formula the surface tension of liquid methanol $\sigma = 22.55$ erg/sq. cm., the gas constant $R = 8.315 \times 10^7$ erg/°/mol., the relative pressure of methanol being designated as P/P_2 , where P_2 is the saturated vapor pressure of the adsorbate at the experimental temperature.

The process of desorption can, as was shown by Zhdanov [8], be described by the above formula, irrespective of whether the pores end blindly or pass right through the granules. The results of the calculations suggest that the pores of our charcoal are largely of the transitional type.

One sample of charcoal with additives, designated AP-1, was prepared by impregnating a weighed sample of AP charcoal with a solution of copper sulfate, so as to give a product containing 4% of copper, after drying. A second sample, designated AP-2, was prepared in the same way, but was treated with aqueous ammonia before drying, and was then heated at 250-300° for 3-6 hours; in this sample the cuprammonium salts underwent decomposition when heated, yielding oxides of copper.

We shall show that water is quite tenaciously retained by the oxides of copper. According to Fricke and Huttig [9] the process of dehydration of dry cupric oxide monohydrate in a stream of dry air proceeds through a series of stages, each with a different water content.

Adsorption and chemisorption of phosphine by recuperational carbon with and without additives

The experiments on adsorption of phosphine were conducted at high temperatures, under conditions excluding the possibility of contamination of the adsorbent by lubricant or mercury vapors. With this object, the training of the adsorbent at 315° and the adsorption of phosphine were conducted with the use of carbon dioxide snow as a coolant, at -78°, both in the Dewar vessel attached at the quartz spring-balance and in that with the U-tube. The most interesting feature of the experiments at sufficiently high temperatures was the oxidation of adsorbed phosphine by oxygen, which was irreversibly adsorbed and chemically bound by both the active charcoal and the copper additive.

a) Chemisorption of phosphine by recuperational carbon without additives, and desorption of the products of surface reaction

We first had to determine to what extent oxygen actively adsorbed or chemically bound by the surface of the adsorbent takes part in the process of chemisorption of phosphine. Special experiments with 100 mg portions of active charcoal were undertaken with this object, at 315°, first measuring the kinetics of adsorption of phosphine (Curve 1, Fig. 2) at 110 mm, and then desorbing (Curve 2, Fig. 2) by means of a portion of degassed active charcoal contained in a vessel cooled in liquid air.

The amount of desorbed product was three times greater than was the amount of adsorbed phosphine, showing that it was a product of reaction of phosphine with oxygen actively adsorbed on the surface of the charcoal. Repeated adsorption of phosphine (Curve 3, Fig. 2) gave very little oxidation, because most of the oxygen had been used up in the first adsorption-desorption cycle. The amount of phosphine adsorbed in the second cycle was considerably greater than in the first, probably because phosphine molecules occupy places on the adsorbent surface previously occupied by oxygen molecules. In the third cycle the amount of desorbed phosphine is exactly equal to that adsorbed, showing that it was recovered unchanged.

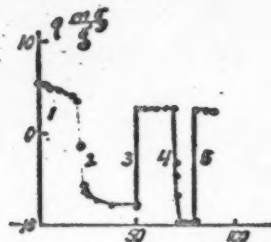


Fig. 2. 1) Adsorption of phosphine at 315°/110 mm by active charcoal, without additives; 2) desorption at 315°; 3) repeated adsorption at 315°/102 mm; 4) desorption at 315°; 5) repeated adsorption of phosphine at 315°/102 mm.

b) Chemisorption of recuperational carbon with copper salt additives and desorption of products of the surface reaction.

High temperature adsorption of phosphine on charcoals with copper additives, and subsequent desorption, proceed quantitatively differently to the case of adsorbent without additives. Fig. 3 shows that total (physical and chemisorption) adsorption of phosphine falls as the temperature rises from 130 to 264° (Curves 1 and 2, Fig. 3), above which it rises with temperature (Curve 4, Fig. 3). These effects are explained by supposing that although physical adsorption falls, specific adsorption (chemisorption) rises with increase in temperature to 320°.

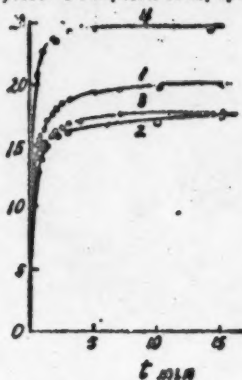


Fig. 3. Adsorption of phosphine on active charcoal AP-2, containing copper additives: 1) at 130°/102 mm; 2) at 264°/102 mm; 3) at 264°/105 mm; 4) at 320°/102 mm.

The Table gives values for adsorption of phosphine, in mg/g, and also for desorption of phosphine and its oxidation products. The same Table also gives results for the amount of adsorbed oxygen, in mg/g, after desorption of phosphine and its oxidation products.

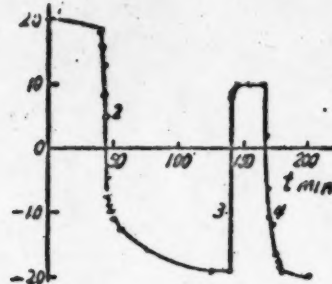


Fig. 4. 1) Adsorption of phosphine at 320°/102 mm on active charcoal AP-2; 2) desorption; 3) repeated adsorption of phosphine at 320°/102 mm; 4) repeated desorption.

At 264° and 320° the desorption process proceeds differently, according to the experimental conditions, judging from the amount of desorbed product, as well as from the amount of oxygen remaining in adsorption (see Table).

It was of interest to ascertain whether the oxygen of adsorbent AP-2 is all used up after the first chemisorption of phosphine at $p = 100$ mm, for which reason special experiments involving repeated adsorption of phosphine were performed. Curve 1 of Fig. 4 represents the process of adsorption of phosphine at 320° on a fresh portion of adsorbent AP-2. Curve 2 represents the process of desorption of the products of chemisorption of phosphine, Curve 3 the process of repeated adsorption of phosphine on the same adsorbent, and Curve 4 the process of repeated desorption. As in the absence of additives, considerably enhanced adsorption (45% more) of phosphine was found in the second adsorption-desorption cycle.

This finding supports the view that the parts of the surface which were in the fresh adsorbent occupied by oxygen molecules were, on repeating adsorption, occupied by phosphine molecules. Thus during primary adsorption of phosphine the first stage of the reaction involves formation of a phosphine-oxygen compound.

TABLE

Temperature, °C	Adsorption of phosphine, mg/g	Desorbed phosphine and its oxidation products, mg/g	Adsorbed oxygen, mg/g	Remarks
320	25	47.5	52.5	Desorbed by means of active charcoal cooled to the temperature of liquid nitrogen.
264	21.4	20.8	53.2	
264	21.4	2.0	22.9	Exhausted by means of a mercury-diffusional pump.

The weight of products desorbed after the second adsorption only slightly exceeds (by 7%) the amount of phosphine adsorbed, showing that nearly all the available oxygen was used up in the chemisorption reaction of the first cycle.

Adsorption of oxygen by active charcoal treated with phosphine at high temperatures

We have shown earlier [1, 2] that raising the temperature of degassing from 17 to 320° leads to an increase in the amount of chemisorbed phosphine from 5.3 to 9.2 ml/g NTP. Experiments on oxidation of chemisorbed phosphine by gaseous oxygen at 17° showed that a considerable part of the phosphine in chemisorption on charcoal previously evacuated at 320° does not undergo oxidation at 17°. Thus, phosphine adsorbed on special parts of the

adsorbent surface, which are made accessible only by treating at high temperature, does not react with gaseous oxygen at 17°.

We shall show that the process of adsorption of phosphine proceeds identically on specimens of adsorbent with added copper sulfate, with or without subsequent treatment with ammonia. The process of adsorption of oxygen is much more rapid on adsorbents treated with ammonia and heated after addition of copper sulfate (Curve 2, Fig. 6), so that their copper is in the form of oxide, than in the case of adsorbents treated with copper sulfate alone. Thus the process of oxidation is greatly accelerated at room temperature on charcoals containing oxides of copper, as compared with those containing sulfate.

The magnitude and the velocity of adsorption of oxygen at 264-320° on charcoal containing copper compounds, and on which phosphine had first been adsorbed and then desorbed, depend very largely on the conditions of desorption. Desorption by means of charcoal cooled in liquid nitrogen leads to elimination of a considerable part of the products of chemisorption of phosphine. Thus at 320° the weight of desorbed product is twice as great as the weight of adsorbed phosphine. An abrupt rise in the velocity and amount of adsorption of gaseous oxygen is observed, as compared with charcoal which had been subjected to desorption effected by means of a mercury-diffusional pump.

The five curves of Fig. 6 represent the kinetics of adsorption of oxygen at ~9.5 mm, at different temperatures. It is evident that Curves 4 and 5, at 320°, differ relatively little from Curve 3, which represents adsorption kinetics at 264°. In all these experiments portions of charcoal AP-2 were first treated with phosphine at a pressure $p = 105$ mm. The method used for desorption of the products of the surface reaction was the same in all cases, viz., exposure to charcoal cooled in liquid nitrogen. The final values for adsorption of oxygen were practically identical in experiments 3, 4, and 5, amounting to $q = 52.5$ mg/g at 320°, and 53.4 mg/g at 264°, irrespective of the large differences in the values for preliminary desorption.

The kinetics of adsorption of oxygen at 264° were very different (Curve 2, Fig. 6) when the products of the surface reaction of phosphine with actively adsorbed oxygen were desorbed by means of evacuation with a mercury-diffusional pump. Adsorption of any contaminants (mercury or lamp-grease vapors) was excluded by means of double or triple traps cooled in liquid air.

Adsorption of oxygen on charcoal AP-2 in the experiments represented by Curves 5, 4 and 3, Fig. 6 is equal to the amount of oxygen needed for total oxidation of the adsorbed phosphine. The experimental results indicate that at 264-320° actively adsorbed phosphine is oxidized

largely by oxygen which is actively adsorbed and chemically bound both by the carbon and by the copper additive. We shall call this the surface reaction of oxidation of phosphine.

The identical results for adsorption of oxygen on activated charcoal at 264 and 320° may perhaps be due to the previously desorbed product being fully oxidized (P_2O_5 , H_2O), since subsequent adsorption of oxygen is unaffected by the presence of this substance.

It may be thought that after partial desorption of the product of chemisorption of phosphine, in total absence of oxygen and at 264-320° it should be possible to obtain a carbon and a metal surface free of actively adsorbed or chemically bound oxygen. Formation of a metal surface free of oxygen is, according to

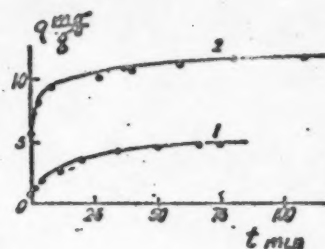


Fig. 5. Adsorption of oxygen: 1) adsorption of oxygen at 19°/10 mm on active charcoal with added copper sulfate, without subsequent treatment with ammonia, and containing 9 mg/g of irreversibly adsorbed phosphine; 2) adsorption of oxygen at 17.5°/9.5 mm by active charcoal AP-2 (treated with ammonia), containing 9.6 mg/g of irreversibly adsorbed phosphine.

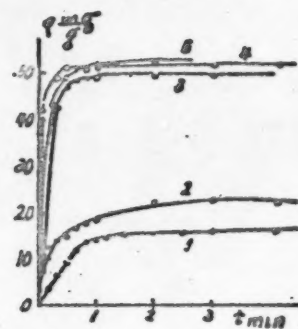


Fig. 6. Adsorption of oxygen at 320° by portions of active charcoal AP-2 on which phosphine had previously been adsorbed and desorbed: 1) at 130°/9 mm; 2) at 264°/10.5 mm; 3) at 264°/9 mm; 4) at 320°/9 mm; 5) at 320°/9.5 mm.

Roginsky [10], possible only in exceptional cases, at the very end of the catalytic process in presence of excess of oxidized substance.

A confirmation of the hypothesis of formation of a surface of high activity with respect to oxygen during the process of stepwise adsorption of phosphine and desorption of the products of its chemisorption at 264-320° is

afforded by the following observation. After desorption at 264° of the product of chemisorption of phosphine the surface of the charcoal AP-2 combines rapidly with considerable amounts of oxygen at pressures of the order of 10^{-4} mm. An increase in weight due to adsorption is observed when the quartz spring-balance is connected with mercury-diffusional and oil vacuum pumps, even when it is protected from access of mercury and oil vapors by three traps cooled in liquid air (Curve 3, Fig. 7).

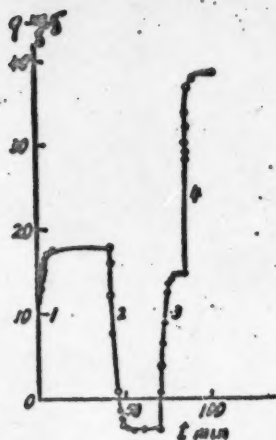


Fig. 7. Adsorption of phosphine on activated charcoal AP-2 at 264°/105 mm; 2) desorption of products of surface reaction of phosphine with adsorbed oxygen; 3) adsorption of oxygen at 264°/ 10^{-4} mm; 4) adsorption of oxygen at 264°/10.5 mm.

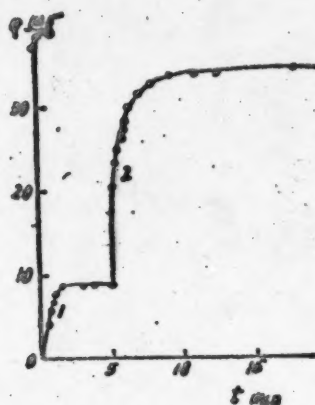


Fig. 8. 1) Adsorption of oxygen at 264°/0.015 mm; 2) adsorption of oxygen at 264°/10 mm.

10^{-4} mm) only a few collisions of oxygen molecules from the gaseous phase are needed for them to become adsorbed.

A special experiment was performed with a portion of charcoal AP-2 on which phosphine had first been adsorbed at $p = 75$ mm and 264°, and the products of surface oxidation of phosphine were then desorbed. Curve 1,

Fig. 8, represents kinetics of adsorption of oxygen at 264°/0.015 mm, and Curve 2 represents kinetics of adsorption of oxygen at $p = 10$ mm.

In connection with the above Bruns' paper [11] on activated adsorption of oxygen by active charcoal, and its role in the catalytic process, is of interest. This author found that only those molecules of oxygen which were loosely bound to the active charcoal displayed catalytic activity, while strongly bound oxygen was unreactive. In our opinion this may be true for the catalytic oxidation of phosphine at room temperature, but at 264-320° practically all of the oxygen, both adsorbed and chemically bound to charcoal AP-2, is used up in the chemisorption of phosphine.

Repeated cycles of stepwise oxidation of phosphine on charcoal containing copper compound additives

Experiments on adsorption and desorption of phosphine on charcoal AP-2 with subsequent adsorption (chemisorption of oxygen from the gaseous phase is of considerable interest, from the point of view of regeneration of active centers of catalysts. Our experiments were conducted at 264 and 320°; Fig. 9 represents two repeated cycles at 320°.

The first cycle of stepwise oxidation is represented by Curve 1, which shows adsorption of phosphine at $p = 102$ mm; Curve 2 represents desorption of products of surface oxidation of phosphine; Curve 3 relates to adsorption of oxygen from the gaseous phase (left-hand branch of Curve 3) and desorption (right-hand branch of Curve 3) before the second cycle. A characteristic feature of this cycle is that maximum desorption of the substance takes place after the surface reaction of phosphine with the oxygen bound to the catalyst.

The second cycle of stepwise oxidation includes the same processes: chemisorption of phosphine (in spite of

the slightly lower pressure than in the first cycle) is represented by Curve 4, and is somewhat greater than in the first cycle.

It is evident that formation of catalyst took place during the first cycle, and was followed by desorption of the product of the surface reaction of phosphine with catalyst oxygen (Curve 5, Fig. 9), and finally by adsorption of oxygen, represented by Curve 6, Fig. 9, which was found to be equal to that found in the first cycle.

The stepwise catalytic process of oxidation of phosphine may thus be regarded as one of alternating reduction and oxidation of the catalyst surface.

Preliminary experiments on chemisorption of phosphine on cuprous and cupric oxide

Experimental study of the role of the carrier of additives catalyzing the reaction of oxidation of phosphine showed that the nature of the surface and the porosity of the carrier play a quite important part in formation of the catalysts. The active charcoal is not only the carrier of the catalytic additive; as we have shown above there is no doubt that chemisorption and subsequent oxidation of phosphine take place at its surface at elevated temperatures. At 18° the process of irreversible specific adsorption takes place only on highly dispersed copper compounds on charcoal. In contradistinction to charcoal AP-2 finely powdered commercial granular cupric and cuprous oxides only weakly adsorb phosphine (~2 mg/g) at room temperature. This may be ascribed in the first place to the much smaller specific surface of these oxides than when they are on the carrier, and in the second place to the activity of these oxides being much lower than when they are on charcoal.

As the temperature rises to 130° adsorption of phosphine on both cuprous and cupric oxide rises sharply, attaining 9-10% of the weight of the catalysts when these were previously treated with oxygen at 130°/30 mm for 20-30 min. The results obtained for kinetics of adsorption of phosphine by cuprous and cupric oxide at 130°/100 mm are shown by the curves of Fig. 10. Adsorption of phosphine on cupric oxide (Curve 2) proceeds much more slowly than for cuprous oxide, under the same conditions, and, in addition, there is an induction period of about 10 minutes during which no adsorption takes place. This is followed by a fairly steep rise in velocity of adsorption, so that the reaction between cupric oxide and phosphine may be regarded as a topochemical process.

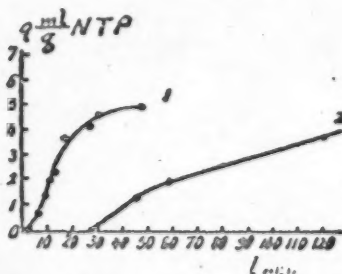


Fig. 11. Adsorption of oxygen by oxides of copper containing chemisorbed phosphine, at 130°: 1) adsorption of oxygen by cuprous oxide at 30 mm; 2) adsorption of oxygen by cupric oxide at 34 mm pressure.

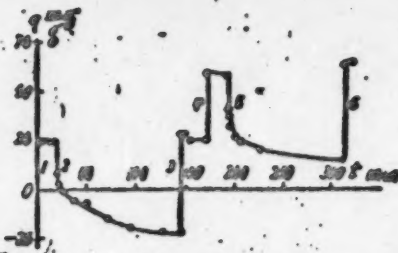


Fig. 9. Repeated cycles of stepwise oxidation of phosphine at 320°, on charcoal AP-2: 1) adsorption of phosphine at 102 mm; 2) desorption; 3) adsorption of oxygen at 9 mm; 4) repeated adsorption of phosphine at 88 mm; 5) desorption; 6) adsorption of oxygen at 88 mm.

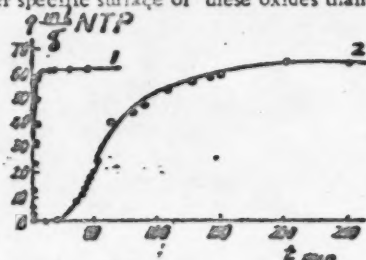


Fig. 10. Adsorption of phosphine by oxides of copper at 130°/100 mm: 1) adsorption of phosphine by cuprous oxide; 2) adsorption of phosphine by cupric oxide.

Curve 1, Fig. 10, represents the kinetics of adsorption of phosphine by cuprous oxide. The process begins as soon as the phosphine is introduced, and it proceeds with uniform speed practically until achievement of equilibrium. After completion of adsorption of phosphine and of desorption (7.1 mg/g were desorbed) we subjected the irreversibly adsorbed phosphine to oxidation. Adsorption of oxygen at 130°/30 mm (Curve 2, Fig. 11) by cupric oxide previously treated with phosphine proceeded more slowly than with cuprous oxide (Curve 1, Fig. 11) also previously treated with phosphine.

The velocity of oxidation of chemisorbed phosphine on cupric oxide is much smaller than on Charcoal AP-2 with copper compound additive. This can be ascribed in the first place to the greater specific surface of copper compounds when adsorbed on charcoal, and in the second to

the specific action of charcoal as a component of the compound catalyst.

Catalytic oxidation of phosphine in mixtures with oxygen in static conditions

Experiments on catalytic oxidation of phosphine mixed with oxygen were conducted at pressures, $p = 0.4$ mm or less, because at higher pressures spontaneous ignition of mixtures of the stoichiometric composition $\text{PH}_3 + 2\text{O}_2$ took place. We used a quartz spring balance for the study of oxidation kinetics for phosphine-oxygen mixtures in the presence of charcoal AP-2 with copper salt, at 18° , at which temperature the oxidation products are retained by the catalyst. In order to minimize pressure changes during experiments of greater duration the $\text{PH}_3 + 2\text{O}_2$ mixture was prepared in a 6-liter flask. The kinetics of the process are illustrated by the curve of Fig. 12.

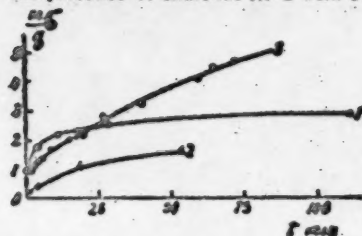


Fig. 12. 1) Adsorption of phosphine at $18.3^\circ/0.1$ mm; 2) adsorption of oxygen at $18.3^\circ/27$ mm; 3) oxidation of phosphine in $\text{PH}_3 + 2\text{O}_2$ mixture at $21^\circ/0.4$ mm.

It is evident that for pressures of about 0.4 mm of the phosphine-oxygen mixture, and at 18° , the activated adsorption process is not a stage limiting the velocity of oxidation of phosphine. Under these circumstances such a stage is that of oxidation of already chemisorbed molecules of phosphine. Calculation of the velocity constants of the reaction of catalytic oxidation from first and second order equations gave values falling steeply and regularly with time; after 60 minutes they were only a tenth of their initial values. This may be ascribed firstly to the non-homogeneity of the catalyst surface, and secondly to retardation of the reaction due to non-volatile oxidation products.

DISCUSSION OF RESULTS

The experimental results allow us to draw certain conclusions, and to advance a reaction scheme for oxidation of phosphine catalyzed by charcoal with copper salt additives, at $18-320^\circ$.

The fastest reaction is that of physical adsorption of phosphine. Simultaneously with physical adsorption we have specific irreversible sorption of phosphine, the rate of which increases with rise in temperature. There is no doubt that catalytic oxidation of phosphine takes place through the stage of specific adsorption. We have shown that presence of specific chemical adsorption is an essential although not a sufficient, condition for the catalytic oxidation of phosphine. Catalytic oxidation of phosphine molecules in chemisorption on copper sulfate (at 20°) proceeds only very feebly, as is also the case for the process (at 20°) at particular locations of active charcoal with oxides of copper, rendered vacant by training at high temperatures in vacuo. It may, from our experiments, be concluded that it is the cuprous form of the copper compound present in the catalysts which is responsible for initiating the reaction of oxidation of phosphine.

At high temperatures chemisorption of phosphine takes place not only on the copper additive, but also at the charcoal surface, which may be regarded under these circumstances as a catalyst of oxidation of phosphine. A complex of phosphine and oxygen formed at the surface undergoes surface oxidation at the expense of oxygen combined with the charcoal surface. The products of surface oxidation may be desorbed as oxides of phosphorus and water, and the adsorbent-additive surface thus liberated possesses considerable reactivity with regard to fixation of gaseous molecular oxygen. The amount of phosphine in chemisorption of the surface of recuperational charcoal itself, at 320° , was only 20% of the amount found with charcoal containing copper salts.

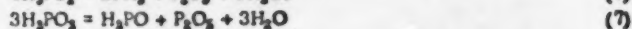
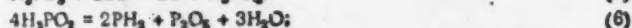
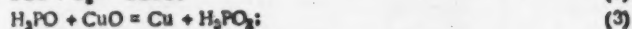
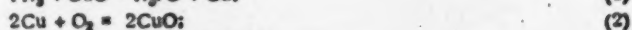
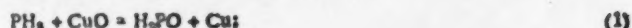
It is of interest to compare the number of molecules of chemisorbed phosphine with the number of copper atoms per gram of catalyst. Active charcoal AP-2 contains 4% of copper, i.e., 40 mg/g, or 3.9×10^{20} atoms of copper. The maximum amount of phosphine in chemisorption at 320° is 24.7 mg/g, of which 5.7 mg is bound by the surface of the charcoal itself. The copper additive has thus been responsible for chemisorption of 19 mg, or 3.39×10^{20} molecules of phosphine. It follows that at 320° each atom of copper present as oxide binds not more than one molecule of phosphine.

It may be concluded from all the available data that the primary specific adsorption of the phosphine molecule involves the participation of the oxygen present on the surface of the charcoal, and its additive, and that subsequent reactions with gaseous oxygen lead to completion of the reaction of oxidation of phosphine, and to the regeneration of the catalyst surface. The catalytic process of oxidation of phosphine should be regarded as a succession of oxidation and reduction processes following rapidly one after the other; at room temperature transfer of oxygen is due to oxides of copper. At elevated temperatures the process of successive oxidations and

reductions takes place not only at the additive surface, but also at the surface of the charcoal itself, which acquires a chemisorbed-oxygen layer.

Chemisorption of phosphine at the charcoal surface at elevated temperatures should be regarded as a reaction of reduction by phosphine of superficial oxide of carbon.

The oxidation products (oxides, not acids) may be desorbed from the catalyst by exposure to charcoal cooled at the temperature of liquid air. Chemisorption of phosphine by copper salt additives may be represented for the particular case of cupric oxide on charcoal by the following schemes:



It is possible that in addition to these reactions part of the phosphine reacts with copper compounds at elevated temperatures to give copper phosphide as an intermediate product; we were able, however, only in a few cases to detect formation of very small amounts of copper phosphide.

SUMMARY

1. Presence of specific chemical adsorption of phosphine on active charcoal with additives is an essential, although not a sufficient, condition for initiation of the process of catalytic oxidation of phosphine.
2. On catalytic charcoal the most firmly chemisorbed molecules of phosphine are only very slowly oxidized by oxygen at room temperature.
3. The cuprous form of copper appears to be responsible for initiation of catalytic oxidation of phosphine.
4. At elevated temperatures the surface of the charcoal itself, without additives, acts catalytically in oxidation of phosphine by atmospheric oxygen.
5. In absence of atmospheric oxygen, and at elevated temperatures, phosphine reacts with oxygen bound to the catalyst AP-2, to give oxides of phosphorus and water. Desorption of these products leaves a surface which adsorbs gaseous oxygen with exceptional avidity.
6. The first stage of chemisorption of phosphine is the formation of a phosphine-oxygen complex at the catalyst surface.
7. The process of catalytic oxidation of phosphine by gaseous oxygen at the surface of active charcoal containing copper oxides involves formation of intermediate compounds, with very rapidly alternating stages of reduction and oxidation of the catalyst. The catalyst is copper oxides at room temperature, while at elevated temperatures the charcoal surface itself can act as a catalyst, without additives.

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ELECTRON ABSORPTION SPECTRA OF POLYSTYRENE AND ITS DERIVATIVES

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The study of the electron spectra of polymers is of fundamental importance, for both theoretical and practical reasons. It would; on the one hand, be of interest to find new spectrum analytical evidence throwing light on the composition and structure of polymers. On the other hand, it would be of interest to elucidate the effect of regularities in the structure of chain polymers on the electron spectrum. As the experimental work of Obreimov, Prikhodko, Rodnikova, and Eichis [1] has shown, the reaction of regularly distributed molecules in crystals leads to significant differences between the spectra of these crystals and of the molecules of which they are composed.

The theory of spectra of molecular crystals was advanced by Davidov [2], who showed that resonance reactions of molecules in crystals, which may be regarded as spreading of the exciting waves (excitons), should lead to the appearance of new, highly polarized lines in the electron spectrum. It might be thought that the same sort of phenomenon is possible also in linear polymers.

EXPERIMENTAL

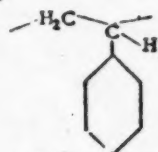
The polymers taken for study were those which had characteristic absorption in the sufficiently close ultra-violet region of the spectrum. We investigated polystyrene and the polymers of some halogen derivatives of styrene, comparing the spectra of the polymers with those of the hydrogenated monomers, taking the spectra under strictly comparable conditions — in solutions in the same solvents, and at the same molar concentrations, calculated on the basis of the monomer unit. The following pairs were studied:

1. Polystyrene — ethylbenzene;
2. Poly-*o*-bromostyrene — *o*-bromotoluene;
3. Poly-2,5-dichlorostyrene — 2,5-dichloroethylbenzene.

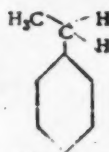
All spectra were in chloroform solution, the concentration for the first pair being 0.019M (calculated for ethylbenzene), and of the same order for the other two pairs. The absorption spectrum of polystyrene in cyclohexane did not differ significantly from that in chloroform. The quartz spectrograph ISP-22 and the quartz photoelectric spectrophotometer SF-11 were used for our study. In the first case quartz cells were taken, the thickness of the layer varying from 0.05 to 10 mm.

Fig. 1 shows the absorption curves for polystyrene and ethylbenzene in chloroform, obtained by the usual methods of photographic photometry. The same Fig. 1 gives the absorption curve for styrene in chloroform. The styrene spectrum differs considerably from those of polystyrene and ethylbenzene, which is a natural consequence of the differences in the chemical structure of these substances.

The spectra of polystyrene and ethylbenzene are practically identical. This is evidence that the spectrum of polystyrene in the given region is determined by electron transfers located in the individual units of the molecule or, more exactly, in the benzene ring:



Polystyrene unit



Ethylbenzene

Small differences between the spectra of polystyrene and

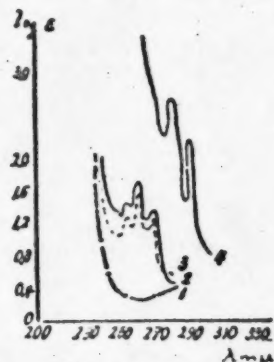
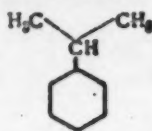


Fig. 1. 1) Chloroform; 2) polystyrene in chloroform; 3) ethylbenzene in chloroform; 4) styrene in chloroform.

ethylbenzene may be connected with differences in their structure. An even better coincidence between the spectra of polystyrene and isopropylbenzene might be expected:



Oscillatory structure is well expressed in the spectrum, the positions of the maxima of the absorption bands being at 269, 262, 255, and 249 $m\mu$. The distances between the maxima correspond to the frequency of vibration of the benzene molecule. Thus, in this case polymerization has no effect on the spectrum in the region of the benzene ring absorption bands. "Collective" spectrum bands, similar to those seen in the spectra of molecular crystals, are not observed in the spectrum of polystyrene. This is evidence that the polystyrene chain is not regularly distributed in space: the polymer is similar to a fluid, but not to a crystal.

The considerable differences between the electron absorption spectra of polystyrene and styrene make it possible to apply a spectrophotometric method to the determination of unpolymerized styrene and polystyrene in their mixtures.

Fig. 2 gives the absorption curves of polybromostyrene and o-bromotoluene in chloroform:

The results obtained are similar to those obtained for polystyrene. The spectra of the polymer and the monomer are practically identical. The positions of the absorption maxima (vibratory structure) for the polymer are at 278, 269, 262, and 255 $m\mu$. Fig. 3 gives the absorption curves of poly-2,5-dichlorostyrene and 2,5-dichloroethylbenzene in chloroform:

The result obtained for this case was more interesting. Here also the spectra of the monomer and the polymer are

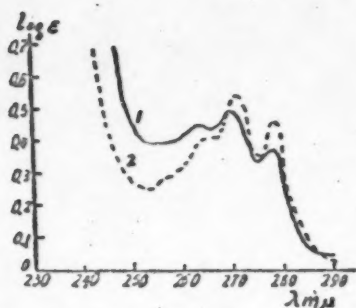
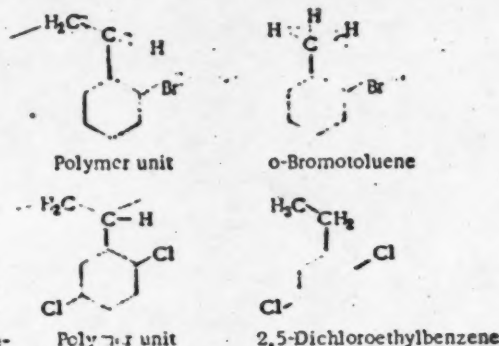


Fig. 2. 1) Poly-o-bromostyrene;
2) o-bromotoluene.

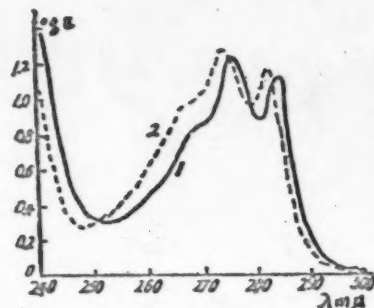


Fig. 3. 1) Poly-2,5-dichlorostyrene;
2) 2,5-dichloroethylbenzene.

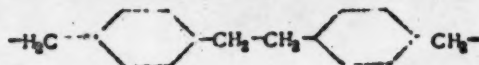
molecular crystals. The regularity in their distribution may be due to interaction of symmetrically disposed dipoles C-Cl. On the other hand, it is possible that the observed shift of the spectrum of the polymer in the direction of greater wave-lengths is determined by ordinary Van der Waals' forces acting within one and the same molecule. The determining factor would again be the dipole moment of the C-Cl bond, and we suppose that the latter assumption is the more probable one. In any case, polymerization here gives rise to a perceptible effect on the electron absorption spectrum.

Experiments performed at low temperatures would be needed for a more profound study of the effect of polymerization on the electron absorption spectrum. Since the results obtained by us give evidence of the non-crystalline nature of the polymers it is not to be expected that the low temperature spectra would manifest any specific effects, such as are found in the spectra of molecular crystals. It might nevertheless be thought that the

The available data do not permit the formulation of any simple explanation of this shift in the spectrum. It may perhaps be due to resonant reaction of the benzene rings, similar to that found in molecular crystals.

low-temperature spectra of the polymers would more clearly reveal the oscillatory structure of the bands.

We also investigated the spectrum of polyphenylenethylenes:



Polyphenylenethylenes, which may be regarded as an isomer of polystyrene, is a dark brown, viscous, resinous substance. It was not found possible, using any of the known chemical methods, to eliminate colored impurities from it. The spectroscopic study should, in particular, have revealed whether the coloration was due to presence of impurities, or to the substance itself. The latter supposition is contradicted by all that is known of the coloration of organic compounds.

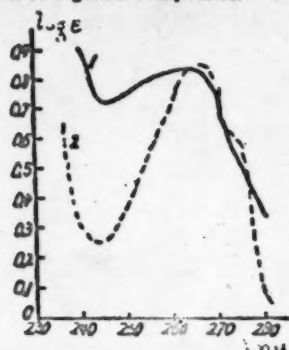
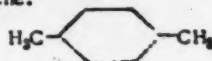


Fig. 4. 1) Polyphenylenethylenes;
2) p-Xylene.

Fig. 4 shows the absorption curves of chloroform solutions of polyphenylenethylenes and p-xylene:



p-Xylene can be regarded as an analog of the individual unit of the polyphenylenethylenes chain. We see that the spectra of the polymer and the monomer resemble each other very closely, both having the same intense absorption band at 264 mμ. Polyphenylenethylenes has no very clear-cut absorption bands in the long wave region. We suppose that the similarity between the spectra of polyphenylenethylenes and p-xylene is evidence that the coloration of the polymer was due to the presence of small amounts of tarry matter formed during polymerization.

We have pleasure in expressing our gratitude to Decent L. V. Smirnov for his help.

SUMMARY

1. A comparison has been made of the ultraviolet absorption spectra of polystyrene and of certain of its derivatives with the spectra of substances having a structure analogous to that of the monomer units of the polymers.
2. Resemblances and differences in the spectra of the polymers and the analogs of their monomer units have been established. The spectrum of polyphenylenethylenes is found to resemble that of p-xylene.

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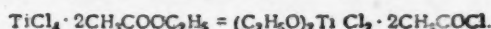
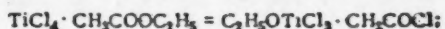
* We take pleasure in thanking V. V. Korshak for supplying us with a specimen of this substance.

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PREPARATION OF TRICHLOROALKOXYTITANES FROM TITANIUM TETRACHLORIDE AND ALCOHOLS

A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina

Friedel and Crafts [1] showed in 1870 that titanium tetrachloride and diethyl ether gave a crystalline product, distillation of which afforded ethyl chloride, diethyl ether, and a second crystalline product, the composition of which corresponded, according to these authors, to the formula $C_2H_5OTiCl_3$. The reaction was again examined later [2], when two double salts were isolated, of the composition $C_2H_5OC_2H_5 \cdot TiCl_4$ and $3C_2H_5OC_2H_5 \cdot 2TiCl_4$, thermal decomposition of which gave trichloroethoxytitane. A further paper was published [3] in which a series of compounds of titanium tetrachloride with esters were described. The author obtained three double compounds of ethyl acetate with titanium tetrachloride, of the compositions $2TiCl_4 \cdot CH_3COOC_2H_5$; $TiCl_4 \cdot CH_3COOC_2H_5$ and $TiCl_4 \cdot 2CH_3COOC_2H_5$, and analogous compounds were obtained with ethyl benzoate. According to the author, the compounds obtained were complex compounds of trichloroethoxytitane and dichlorodiethoxytitane, of the types:



This author based his views on the fact that trichloroethoxytitane obtained by him, apparently by the Friedel-Crafts method, gave the same compound with titanium tetrachloride and acetyl chloride as was obtained from an equimolecular mixture of titanium tetrachloride and ethyl acetate.

It seems to us to be unlikely that formation of trichloroethoxytitane, which requires fairly drastic reaction conditions, could result from the mere mixing of the reagents. More probably, double compounds of titanium tetrachloride with esters are produced in these conditions. As for the reaction of trichloroethoxytitane with acetyl chloride, this may proceed as follows:



A fairly recent paper [4] mentions an attempt at preparation of trichloroethoxytitane, apparently by the reaction of dichlorodiethoxytitane with acetyl chloride, but the expected product was not obtained.

We thus see that only one of the trichloroalkoxytitanes, viz., trichloroethoxytitane, has up till now been prepared [2]. The reaction whereby it was prepared is a complex one, giving rise to a number of by-products, and suffers from the disadvantage that many ethers (such as ethers of sec.- and tert-alkyls) are not readily available.

Luchinsky [5], in studying the reaction of titanium tetrachloride with phenols, found that phenol and m-nitrophenol gave trichloroaryloxytitanes, whereas p-chlorophenol and o- and p-nitrophenol gave dichloroaryloxytitanes. This author did not investigate why certain phenols replaced only one chlorine atom, whereas others replaced two.

As part of our study of aliphatic derivatives of titanium [6,7,8] we decided to work out a method of synthesis of trichloroalkoxytitanes from titanium tetrachloride and alcohols. All the published work on the direct action of alcohols on titanium tetrachloride has been done under conditions of large excess of alcohol [4], and the sole products were the double compounds of dichlorodialkoxytitanes with alcohols, $(RO)_2TiCl_2 \cdot ROH$. Since it was obvious that this reaction must have passed through the stage of trichloroalkoxytitane, we thought that if it were

to be conducted with excess of titanium tetrachloride it should give trichloroalkoxytitanes as the main product.

This was found to be the case; the sole product obtained by heating ethanol with a ten-fold excess of titanium tetrachloride was trichloroethoxytitanane. We found that the reaction was more conveniently conducted when inert solvents were added, when only a relatively small excess of titanium tetrachloride needs to be taken. The solvents tried were carbon tetrachloride and light petroleum. It is essential that the solution of the alcohol should be added to titanium tetrachloride, and not vice versa. After mixing the solutions the systems were boiled for several hours, until evolution of hydrogen chloride was complete, the solvent was distilled off, and the residue was fractionally distilled under reduced pressure.

This method for the synthesis of trichloroalkoxytitanes is convenient and simple, and gives quantitative yields of products. The method was tried with primary n- and isoalcohols, and with alcohols with substituents in the chain.

The products obtained were trichloro-ethoxytitanane, -n-propoxytitanane, -isobutoxytitanane, -isoamylxytitanane, and -n-hexoxytitanane, which are crystalline, hygroscopic, readily hydrolyzable substances. They have low melting points, and can be distilled in vacuum without decomposition. They are readily soluble in diethyl ether and benzene, and more sparingly soluble in carbon tetrachloride, light petroleum, or chloroform.

Trichloro- β -methoxyethoxytitanane, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OTiCl}_3$, differs from the above products in having a much higher m.p., and in its insolubility in ordinary solvents.

EXPERIMENTAL

All the reactions were conducted with scrupulously dried reagents, and under conditions such that access of atmospheric moisture was excluded.

Preparation of trichloro-n-propoxytitanane ($\text{n-C}_3\text{H}_7\text{OTiCl}_3$). A solution of 30 g (0.5 mole) of thoroughly dried n-propanol in 200 ml of light petroleum was added from a dropping funnel to a solution of 142.5 g (0.75 mole) of titanium tetrachloride in 300 ml of light petroleum (fraction boiling at 50-80°) in a flask fitted with a phosphorus pentoxide tube. Vigorous evolution of hydrogen chloride proceeded for about an hour, after which the solution was boiled on the water bath. Part of the solvent was then distilled off, and the residue was cooled in a freezing mixture. The precipitate formed was distilled at 11 mm, boiling at 83-85°; when redistilled the b.p. was 100-102° at 23 mm. The yield of crude product was 103 g (96.5%).

Found %:	C 16.79;	H 3.19;	Cl 49.64;	Ti 22.10;
$\text{C}_3\text{H}_7\text{OTiCl}_3$, Calculated %:	C 16.88;	H 3.31;	Cl 49.86;	Ti 22.45.

Trichloro-n-propoxytitanane is a light yellow, crystalline substance, m.p. 65-67° (sealed capillary). It is hygroscopic, and is readily hydrolyzed.

Preparation of trichloro-ethoxytitanane $\text{C}_2\text{H}_5\text{OTiCl}_3$. The procedure was as above. A solution of 23 g (0.5 mole) of absolute ethanol in 200 ml of light petroleum (b.p. 50-80°) was added gradually to 142 g (0.75 mole) of titanium tetrachloride in 300 ml of light petroleum, and the mixture was boiled on the water bath for 8 hrs until evolution of hydrogen chloride had ceased. The mixture was left until the next morning, when the supernatant liquid was decanted off from the precipitate which had formed, and most of the solvent was distilled off from it. The residue was cooled in freezing mixture, when a further portion of precipitate separated from it, giving a total yield of 87 g (87.5%). The light yellow, crystalline product was hygroscopic, and was readily hydrolyzable. It boiled at 185-186°/760 mm; the published value of the b.p. of $\text{C}_2\text{H}_5\text{OTiCl}_3$ [2] is 186-188°.

Found %:	C 12.09;	H 11.85;	Cl 53.21;	Ti 23.90;
$\text{C}_2\text{H}_5\text{OTiCl}_3$, Calculated %:	C 12.04;	H 12.53;	Cl 53.37;	Ti 24.03.

Preparation of trichloroisobutoxytitanane $\text{iso-C}_4\text{H}_9\text{OTiCl}_3$. The procedure was as before, except that carbon tetrachloride was taken as the solvent. A solution of 24.7 g (0.33 mole) of isobutanol in 100 ml of carbon tetrachloride was added gradually to 95 g (0.5 mole) of titanium tetrachloride in 125 ml of carbon tetrachloride, and the mixture was boiled for 9 hours. The crystalline product separating from the cooled solution boiled at 92-94° at 9 mm, and the m.p. of the distilled product (sealed capillary) was 81-83°.

Found %:	C 21.39;	H 3.81;	Cl 46.42;	Ti 21.14;
$\text{C}_4\text{H}_9\text{OTiCl}_3$, Calculated %:	C 21.13;	H 3.99;	Cl 46.78;	Ti 21.06.

The yield of crude product was practically theoretical. Trichloroisobutoxytitanate is a hygroscopic crystalline substance, readily hydrolyzable.

Preparation of trichloroisobutoxytitanate $\text{iso-C}_4\text{H}_9\text{OTiCl}_3$. The same procedure was applied as before. A solution of 44 g (0.5 mole) of isoamyl alcohol in 200 ml of light petroleum was added to 142.5 g (0.75 mole) of titanium tetrachloride in 300 ml of light petroleum, and the mixture was boiled for 5 hrs on the water bath, until evolution of hydrogen chloride ceased. The cooled solution gave 115 g of product (95.5% of theory). The light yellow crystalline product is hygroscopic and readily hydrolyzable; it boils at 110-111°/17 mm, and the distilled substance melts at 50-60° (sealed capillary).

Found %: C 24.91; 24.63; H 4.88; 4.95; Ti 19.52; 19.58
 $\text{C}_4\text{H}_9\text{OTiCl}_3$, Calculated %: C 24.87; H 4.59; Ti 19.84.

Preparation of trichloro-n-hexoxytitanate $\text{n-C}_6\text{H}_{13}\text{OTiCl}_3$. The procedure was as above. A solution of 40 g (0.39 mole) of n-hexanol in 150 ml of light petroleum was added gradually to 112 g (0.58 mole) of titanium tetrachloride in 150 ml of light petroleum. A precipitate formed as soon as the reagents were mixed. The mixture was boiled for 3 hrs, until evolution of hydrogen chloride had ceased.

Trichloro-n-hexoxytitanate is a light yellow crystalline substance, and is hygroscopic and readily hydrolyzable. It boils at 120-122°/8 mm, and the m.p. of the twice-distilled product is 47.5-49° (sealed capillary). The yield is practically quantitative.

Found %: Cl 40.86; 41.33; Ti 18.70; 18.90
 $\text{C}_6\text{H}_{13}\text{OTiCl}_3$, Calculated %: Cl 41.65; Ti 18.75.

Preparation of trichloro- β -methoxyethoxytitanate $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OTiCl}_3$. The method was the same as before. A solution of 38 g (0.5 mole) of β -methoxyethanol in 125 ml of carbon tetrachloride was added gradually to 142.5 g (0.75 mole) of titanium tetrachloride in 150 ml of carbon tetrachloride, and the mixture was boiled for 4 hrs. The precipitate separating was collected; it is insoluble in light petroleum, carbon tetrachloride, benzene, or diethyl ether. It was analyzed after repeated washing with light petroleum (30-50°) and diethyl ether, and drying in vacuum.

Found %: C 15.80; 15.84; H 3.16; 3.22; Cl 46.33; 46.40; Ti 20.50; 20.40
 $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OTiCl}_3$, Calculated %: C 15.71; H 3.08; Cl 46.38; Ti 20.88

The product slowly distills over when heated on an oil bath, at 160-180°/5 mm, and the distilled substance melts at 164-166° (sealed capillary). The yield of crude product is close to the theoretical.

SUMMARY

1. A new method for the synthesis of trichloroalkoxytitanates, based on the reaction of alcohols with titanium tetrachloride, is described.
2. The following new products were obtained: trichloro-n-propoxytitanate, -isobutoxytitanate, -isoamloxytitanate, -n-hexoxytitanate, and - β -methoxyethoxytitanate.

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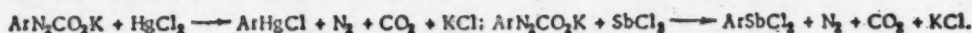
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SYNTHESIS OF AROMATIC ARSENIC-ORGANIC COMPOUNDS THROUGH ARYLAZO-CARBOXYLIC SALTS

O. A. Reutov and Yu. G. Bundel

Nesmeyanov [1] and Pritsina and one of us [2] have elaborated a method of synthesis of aromatic compounds of mercury and antimony, by the reaction of potassium arylazocarboxylates with mercuric chloride or antimony trichloride, as follows:



This method has in the present paper been extended to the synthesis of arsenic-organic compounds.

As was expected, arylazocarboxylic salts readily reacted with cold solutions of arsenic trichloride in acetone or ethyl acetate, giving the appropriate arsenic-organic compounds, from potassium phenylazo-, p-tolylazo-, p-bromophenylazo-, p-nitrophenylazo-, β -naphthylazo-, and 2,4,6-tribromophenylazo-carboxylate.

Reaction of arylazocarboxylic acid salts with arsenic trichloride

Reaction temperature 18-20°; solvent-acetone; excess of AsCl_3 50%

Serial No.	Arylazocarboxylic acid salt	Reaction products, %			Total yield, %
		ArAsO	$(\text{Ar}_2\text{As})_2\text{O}$	$\text{ArAs}(\text{OH})_2$	
1	$\text{C}_6\text{H}_5\text{-N=N-C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OK} \end{smallmatrix}$	42	21	-	63
2	$p\text{-CH}_3\text{C}_6\text{H}_4\text{-N=N-C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OK} \end{smallmatrix}$	32	20	-	52
3	$p\text{-BrC}_6\text{H}_4\text{-N=N-C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OK} \end{smallmatrix}$	47	34	-	81
4	$p\text{-O}_2\text{NC}_6\text{H}_4\text{-N=N-C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OK} \end{smallmatrix}$	-	-	64	64
5	$\beta\text{-C}_{10}\text{H}_7\text{-N=N-C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OK} \end{smallmatrix}$	-	-	30	30
6	$2,4,6\text{-Br}_3\text{C}_6\text{H}_2\text{-N=N-C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{OK} \end{smallmatrix}$	36	-	-	36

A detailed study of the reaction between potassium phenylazocarboxylate and arsenic trichloride showed that the optimum conditions were gradual addition of the salt to acetone solution of arsenic trichloride (50% excess) at room temperature, with constant stirring. The same conditions were applied to all the arylazocarboxylates with arsenic trichloride.

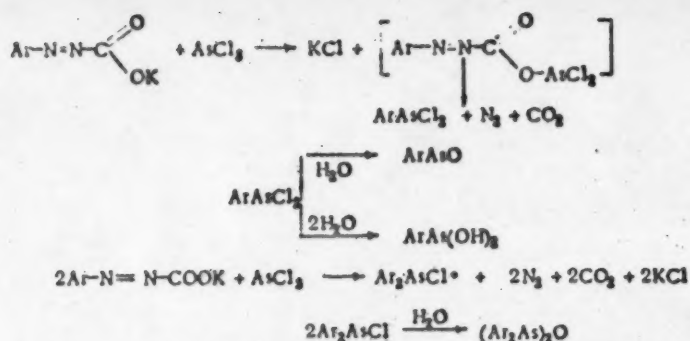
Separation of the arsenic-organic compounds formed was effected after their alkaline hydrolysis* into the corresponding arylarsine oxides or arylarsenious acids. The results are given in the Table.

As is evident from the Table, the reaction products are monoarylsarsine oxides, diarylsarsine oxides, and monoarylsarsenious acids, i.e.,

exclusively trivalent arsenic derivatives; this differs from the results for the synthesis of antimony-organic compounds through arylazocarboxylic salts [2], where both ter- and quinque-valent antimony derivatives are formed.

Formation of monoarylsarsine oxides, arylarsenious acids, and diarylsarsine oxides appears to proceed according to the following schemes:

* 2,4,6-Tribromophenyldichloroarsine was hydrolyzed by water without addition of alkali.

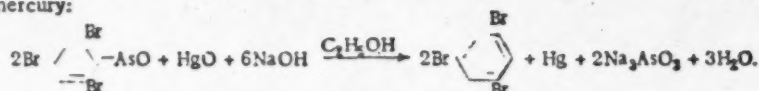


It is of interest that 2,4,6-tribromophenyldichloroarsine is given by the reaction between potassium 2,4,6-tribromophenylazocarboxylate and arsenic trichloride, since attempts at preparing analogous mercury-organic [1] and antimony-organic [2] compounds were unsuccessful. It seems that tribromophenyl compounds of mercury or antimony cannot be formed, owing to steric hindrance of the two bromine atoms in the ortho-position. Owing to the smaller size of the As atom (the Van der Waals radii of Hg, Sb, and As atoms are respectively 2.3, 2.2, and 2.0 Å) steric hindrance is much smaller, or even entirely absent; moreover, an important factor connected with formation of the tribromophenyl derivative of arsenic is the high stability of the arsenic-carbon link, in general.

Although aromatic arsenic-organic compounds generally yield mercury-organic compounds [3] when treated with mercuric oxide in alkaline media, according to the equation

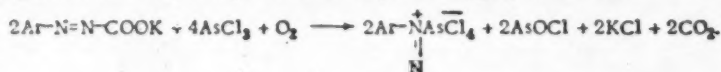


2,4,6-tribromophenylarsine oxide reacts differently under these conditions, forming 1,3,5-tribromobenzene and metallic mercury:



We found that the addition of zinc dust to the reaction mixture obtained from potassium phenylazocarboxylate or p-bromophenylazocarboxylate and AsCl_3 gives vigorous evolution of nitrogen. This is evidence that the products of reaction between arylazocarboxylates and AsCl_3 include not only arsenic-organic compounds, but also double salts of aryl diazonium chloride with arsenic trichloride. **

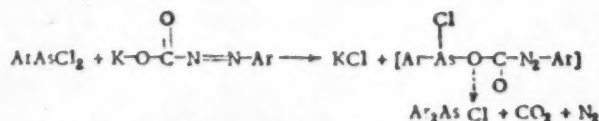
Formation of ArN_2Cl , AsCl_3 , as also formation of Mey salts in the reaction between $\text{ArN}_2\text{CO}_2\text{K}$ and SbCl_3 [3], proceeds with participation of atmospheric oxygen, as follows:



This reaction proceeds much more readily than does the analogous reaction with SbCl_3 ; the zinc dust test shows the presence of the double diazonium salt in the reaction mixture immediately after addition of $\text{ArN}_2\text{CO}_2\text{K}$ to the AsCl_3 solution, whereas in the case of SbCl_3 contact of the reaction solution with atmospheric oxygen for several hours is necessary. If the reaction between $\text{ArN}_2\text{CO}_2\text{K}$ and AsCl_3 is conducted in a stream of nitrogen, so as to exclude access of atmospheric oxygen, the double diazonium salt is not formed.

We were not able to isolate $\text{ArN}_2\text{Cl} \cdot \text{AsCl}_3$ in a pure state from the reaction mixture by the same method as was applied to isolation of Mey's salts in the reaction between arylazocarboxylates and antimony trichloride [2].

* It is possible that diaryldichloroarsine is formed by the reaction between aryl dichloroarsine and potassium arylazocarboxylate:



** Salts of arylazocarboxylic acids are not decomposed by zinc dust.

This result was not, however, unexpected, since the double salts of p-tolyldiazonium chloride and AsCl_3 described in the literature ($\text{C}_7\text{H}_7\text{N}_2\text{Cl} \cdot \text{AsCl}_3$ and $\text{C}_7\text{H}_7\text{N}_2\text{Cl} \cdot 2\text{AsCl}_3$) are very unstable [4]. In order to study the properties of the double salt of phenyldiazonium chloride and AsCl_3 we prepared this compound in acetone solution by the reaction:



precipitating the $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \cdot \text{AsCl}_3$ from solution by addition of ether. The solid product can be stored for several hours without decomposition, but it decomposes very quickly in acetone or ethyl acetate solution, and in particular in contact with ether.**

We were able to demonstrate the formation of the double salt of $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ and AsCl_3 in the reaction between $\text{C}_6\text{H}_5\text{N}_2\text{CO}_2\text{K}$ and AsCl_3 in the following way. The reaction between potassium phenylazocarboxylate and arsenic trichloride was conducted at low temperature in toluene solution***, passing a stream of air. The precipitate formed, consisting of KCl , AsOCl_2 , and $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \cdot \text{AsCl}_3$, was collected by filtration, and was washed with small portions of acetone. The double salt of phenyldiazonium chloride and arsenic trichloride, which is dissolved out by the acetone, was converted by the action of mercuric chloride into the much more stable salt of phenyldiazonium chloride and mercuric chloride, which served for identification:



EXPERIMENTAL

1. Reaction of potassium phenylazocarboxylate with arsenic trichloride. 7 g of potassium phenylazocarboxylate (for preparation see [5] and [6]) was added during 10 min. to a solution of 10.2 g of arsenic trichloride (50% excess) in 150 ml of dry acetone at room temperature, with stirring, which was continued for a further 20 min. The inorganic precipitate which separates (4.1 g) was collected and washed with small portions of acetone. The solvent was evaporated off from the filtrate*** under reduced pressure, at 35-40°. The residual brown mass was twice washed with cold 1:1 hydrochloric acid (30 and 15 ml) and with water (15 ml), and was then heated at 90-100° with 15 ml of 40% KOH in a porcelain basin. The hot mixture was filtered through a glass filter, on which a residue of 0.8 g of diphenylarsine oxide, contaminated with tarry matter, remained; it melted at 86-88° after recrystallization from light petroleum.

Cooling the filtrate in freezing mixture gave a precipitate consisting of potassium chloride and diphenylarsine oxide, from which KCl was eliminated by washing with water, leaving 0.15 g. of diphenylarsine oxide, the combined yield of which was thus 0.95 g (21% of theory); the m.p. was 88-90°, published m.p. 91-92° [7].

Addition of saturated ammonium chloride solution to the filtrate gave a precipitate of 2.6 g (42% of theory) of phenylarsine oxide, which was purified by repeated dissolution in chloroform and precipitation with ether. The m.p. was 127-130°; published values for the m.p. 119-121° [7] and 142-144° [8].

Found %: C 42.65; 42.75; H 2.80; 3.04

$\text{C}_6\text{H}_5\text{AsO}$. Calculated %: C 42.87; H 3.00

Found %: As 45.15

$\text{C}_6\text{H}_5\text{AsO}$. Calculated %: As 44.61

The combined yield of arsenic-organic compounds amounted to 63% of the theoretical.

* In reality an approximately equimolecular mixture of $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \cdot \text{AsCl}_3$ and $(\text{C}_6\text{H}_5\text{N}_2\text{Cl})_2 \cdot \text{AsCl}_3$ is formed.

** It is very probable that $\text{ArN}_2\text{Cl} \cdot \text{AsCl}_3$ is formed not only in the reaction between $\text{C}_6\text{H}_5\text{N}_2\text{CO}_2\text{K}$ or $p\text{-BrC}_6\text{H}_4\text{N}_2\text{CO}_2\text{K}$ and AsCl_3 , but also in all other cases; their not being shown by the zinc dust test may be due to their decomposition in the first stage of the reaction between $\text{ArN}_2\text{CO}_2\text{K}$ and AsCl_3 .

*** Toluene was chosen as the solvent because the double diazonium salt is insoluble in it, and separates out as a precipitate. A low temperature was taken in order to retard the reaction between $\text{C}_6\text{H}_5\text{N}_2\text{CO}_2\text{K}$ and AsCl_3 , and hence to prolong the time of contact of the reaction mixture with atmospheric oxygen.

**** Addition of zinc dust to the filtrate gives energetic evolution of nitrogen.

2. Reaction of potassium p-tolylazocarboxylate with arsenic trichloride. 9.5 g of potassium p-tolylazocarboxylate (for preparation see [5]) was added during 10 min. to a solution of 12.5 g (50% excess) of arsenic trichloride in 200 ml of dry acetone at room temperature, with constant stirring, which was continued for a further 20 min. The inorganic precipitate (I) was collected and washed with small portions of acetone; it weighed 4.5 g. The solvent was removed from the filtrate by evaporation at 25-30° under reduced pressure, and the pasty brown residue was twice washed with cold 1:1 hydrochloric acid (30 and 15 ml), and was then added drop by drop to 30 ml of 50% KOH. The mixture solidified after a few minutes, when it was passed through a glass filter, giving precipitate (II), which was extracted on the filter with 80 ml of cold water. Addition to the extract of saturated aqueous NH_4Cl gave a precipitate of p-tolylarsine oxide, which was collected and washed with small portions of water; yield 2.2 g (32%). After washing with ether and recrystallizing from ethanol the product melted at 167-169°; published m.p. 156-158° [9].

Found %: C 46.30; 46.48; H 4.31; 4.33
 $\text{C}_7\text{H}_7\text{AsO}$. Calculated %: C 46.19; H 3.88

Some di-p-tolylarsine oxide, contaminated with tarry matter, remained on the filter after treatment of precipitate (II) with water. Three recrystallizations from light petroleum gave 1.2 g (20% of theory) of product of m.p. 103-105°; published m.p. 98° [10].

Found %: C 63.12; H 5.50
 $\text{C}_{11}\text{H}_{11}\text{As}_2\text{O}$. Calculated %: C 63.42; H 5.10.

The combined yield of arsenic-organic compounds was 3.4 g (52% of theory).

3. Reaction of potassium p-bromophenylazocarboxylate with arsenic trichloride. 4.5 g of potassium p-bromophenylazocarboxylate (for preparation see [11]) was added during 10 min. to a solution of 4.6 g of arsenic trichloride (50% excess) in 100 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate was collected (3.1 g) and washed with small portions of acetone. The solvent was removed from the filtrate • by evaporation at 25-30° under reduced pressure, and the residue was twice washed with cold 1:1 hydrochloric acid (25 and 10 ml), and then with water (10 ml), after which it was treated with 30 ml of 1:3 aqueous KOH. The mixture was filtered through glass, giving a residue of 1.0 g (34% of theory) of di-p-bromophenylarsine oxide, m.p. 157-159° after recrystallization from chloroform. The product, which has not previously been reported, is colorless, readily soluble in chloroform and acetone, moderately soluble in ethanol, and sparingly soluble in ether.

Found %: C 36.48; 36.34; H 2.39; 2.17
 $\text{C}_{14}\text{H}_8\text{OBr}_2\text{As}_2$. Calculated %: C 36.49; H 2.04

Addition to the filtrate of 30 ml of saturated aqueous ammonium chloride gives 2.0 g (47% of theory) of p-bromophenylarsine oxide, m.p. 239-240°, after recrystallization from ethanol; published m.p. 259-261° [11].

Found %: C 29.13; 29.16; H 1.71; 1.88
 $\text{BrC}_6\text{H}_4\text{AsO}$. Calculated %: C 29.18; H 1.63.

The combined yield of arsenic-organic compounds was 3.0 g (81% of theory).

4. Reaction of potassium p-nitrophenylazocarboxylate with arsenic trichloride. 8 g of potassium p-nitrophenylazocarboxylate (for preparation see [11]) was added during 10 min. to 9.3 g (50% excess) of arsenic trichloride in 150 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate (3.5 g) was collected and washed on the filter with small portions of acetone. The solvent was evaporated off from the filtrate at 25-30°, under reduced pressure, and the residue was twice washed with cold 1:1 hydrochloric acid, and then with water (15 ml) after which it was treated with 30 ml of 1:5 aqueous KOH. The solid hydrolysis product, which was p-nitrophenylarsenious acid, was collected and washed with water; yield 4.5 g (64% of theory). It was purified by repeated dissolution in concentrated aqueous KOH, and precipitation with hydrochloric acid, followed by thorough washing with ether. p-Nitrophenylarsenious acid is a light brown substance which decomposes explosively when heated; it is sparingly soluble in organic solvents. According to the literature [13] it is a brown substance, soluble in alkalis, exploding when heated.

• Addition of zinc dust to the filtrate causes vigorous evolution of nitrogen.

Found %: C 30.84; 30.75; H 2.43; 2.26
 $\text{C}_2\text{NC}_8\text{H}_7\text{As}(\text{OH})_2$ Calculated %: C 31.18; H 2.62

5. Reaction of potassium β -naphthylazocarboxylate with arsenic trichloride. 7.5 g of potassium β -naphthylazocarboxylate* was added during 10 min to a solution of 1 g of arsenic trichloride (50% excess) in 150 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate separating (4 g) was collected and washed with acetone, and the solvent was evaporated off from the filtrate at 25-30° under reduced pressure. The residue was washed with cold 1:1 hydrochloric acid (50 and 25 ml) and with water (25 ml), and was then treated with dilute aqueous KOH (1:10) for 1 hr. As the β -naphthylarsenious acid so obtained is difficultly soluble in organic solvents it was purified by thorough washing with alcohol and ether; the m.p. was 140°. Yield 2.5 g (30%).

Found %: C 50.36; H 3.31
 $\text{C}_{18}\text{H}_7\text{As}(\text{OH})_2$ Calculated %: C 50.84; H 3.83

6. Reaction of potassium 2,4,6-tribromophenylazocarboxylate with arsenic trichloride. 3.7 g of potassium 2,4,6-tribromophenylazocarboxylate (for preparation see [14]) was added during 10 min to a solution of 4.7 g of arsenic trichloride (50% excess) in 125 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate separating (1.3 g) was collected and washed with acetone, and the solvent was evaporated off from the filtrate at 25-30° under reduced pressure. The residue solidified when cooled in a freezing mixture, and it was washed with 50 ml of 1:1 HCl and with water, collected on the filter, dried, and extracted with a large volume of ether. The residue after evaporation of the ether extract is tribromophenylarsine oxide, contaminated with tribromobenzene and tarry matter. 2,4,6-Tribromophenylarsine oxide was recrystallized from a large volume of ethanol, and was washed with ether; it is a colorless substance, difficultly soluble in the ordinary organic solvents, m.p. 215-220°, yield 1.55 g (36% of theory). It has not previously been described.

Found %: C 18.05; 17.58; H 0.56; 0.58; Br 51.39; 50.64
 $\text{C}_6\text{H}_2\text{OBr}_3\text{As}$ Calculated %: C 17.78; H 0.50; Br 50.26

7. Preparation of the double salt of phenyldiazonium chloride and arsenic trichloride. 10 g of the double salt of phenyldiazonium chloride and ferric chloride (for preparation see [15]) was dissolved in the least volume of acetone, and 8 g of arsenic trichloride was added to the solution. The mixture was cooled in a freezing mixture and ether was added until no further precipitate formed. The precipitate was collected and washed with cold acetone. It does not contain any $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \cdot \text{FeCl}_3$ or FeCl_3 (tested with KCNS); it is readily soluble in water, sparingly soluble in acetone and ethyl acetate, and difficultly soluble in benzene and ether, although it readily decomposes when in contact with ether. It is unstable, marked decomposition being evident after 24 hrs. Its m.p. is 89-90° (decomposition).

Found %: N 10.81; 10.75

Analysis showed that the product is a mixture of two substances, $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \cdot \text{AsCl}_3$ (calc. N content 8.70%) and $(\text{C}_6\text{H}_5\text{N}_2\text{Cl})_2 \cdot \text{AsCl}_3$ (calc. N content 12.1%).

8. Reaction of 2,4,6-tribromophenylarsine oxide with mercuric oxide in alkaline media. A hot solution of 0.15 g of 2,4,6-tribromophenylarsine oxide in 1 ml of ethanol was added to a hot solution of 0.13 g of mercuric chloride in 1.5 ml of ethanol, followed by 0.75 ml of boiling aqueous 5 N sodium hydroxide, and the mixture was boiled for 2 min, and filtered off from the precipitate of metallic mercury. 7 ml of water was added to the cooled filtrate, and the precipitate (0.05 g) of 1,3,5-tribromobenzene, m.p. 118-120°, was collected; the published m.p. is 115-121° [16]. The product gave no m.p. depression with a specimen of tribromobenzene.

9. Conversion of the double salt of phenyldiazonium chloride and arsenic trichloride, formed in the reaction between $\text{C}_6\text{H}_5\text{N}_2\text{CO}_2\text{K}$ and AsCl_3 , into a double salt of phenyldiazonium chloride and mercuric chloride. 8 g of potassium phenylazocarboxylate was added to a solution of 23 g (3-fold excess) of arsenic trichloride in toluene at -15°; evolution of gas was not observed. The temperature of the reaction mixture was raised during an hour to 20°, passing a stream of air through it (the reaction begins to proceed when the temperature of the mixture reaches 5°). The precipitate was collected after completion of the reaction; it consists of potassium chloride, arsenic oxychloride, and double salt of phenyldiazonium chloride and arsenic trichloride, and weighed 5.5 g. The precipitate was washed with benzene, and the double salt was extracted with 20 ml of acetone, when the residue weighed 3.5 g. A concentrated solution of 3 g of HgCl_2 in acetone was added to the acetone extract,

* Prepared by hydrolysis with alcoholic alkali of ethyl β -naphthylazocarboxylate.

followed by ether until no more white precipitate formed, and the double salt so obtained was twice reprecipitated from acetone with ether, to give a colorless substance, which gradually decomposes when heated at 100-130°. A suspension of the product in acetone or ethyl acetate is decomposed by addition of zinc dust. According to the literature [17] the double salt is a white, crystalline, infusible substance, which gradually decomposes when heated.

Found %: N 7.20; 7.02
 $C_6H_5N_2Cl \cdot HgCl_2$. Calculated %: N 6.80

10. Reaction of potassium phenylazocarboxylate with arsenic trichloride in acetone, in an atmosphere of nitrogen. A suspension of 5 g of potassium phenylazocarboxylate in 100 ml of dry acetone was placed in a flask fitted with a dropping-funnel, and air was swept out by passing a stream of nitrogen for 20 minutes. A solution of 7.5 g of arsenic trichloride in 50 ml of dry acetone was then added gradually from the dropping funnel, without interrupting the flow of nitrogen, and with stirring. After completion of the reaction, the zinc dust test was negative, showing that the reaction mixture did not contain double salt of phenyldiazonium chloride and arsenic trichloride (gases not evolved). After a short contact of the mixture with air addition of zinc dust is followed by evolution of nitrogen, showing that the double diazonium salt has been formed.

SUMMARY

1. A method for the synthesis of aromatic arsenic-organic compounds through arylazocarboxylic salts is described.
2. The mechanism of the reactions involved is discussed.
3. It has been shown that arylazocarboxylic salts with arsenic trichloride in presence of air readily undergo conversion into double salts of arylidiazonium chloride and arsenic trichloride.

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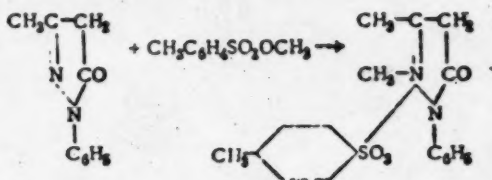
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* See Consultants Bureau translation, p. 103.

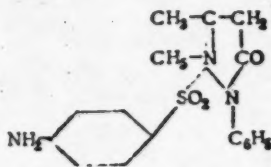
NEW DATA ON THE CHEMISTRY OF PYRAZOLONE DERIVATIVES

V. M. Rodionov and A. M. Fedorova

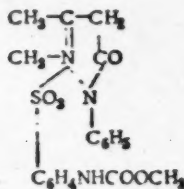
One of us [1] was able, during the course of a study of the conditions of synthesis of pyrazolone derivatives, to obtain in good yield the metho-*p*-toluenesulfonate of phenylmethylpyrazolone, by heating it with an equimolecular amount of methyl *p*-toluenesulfonate:



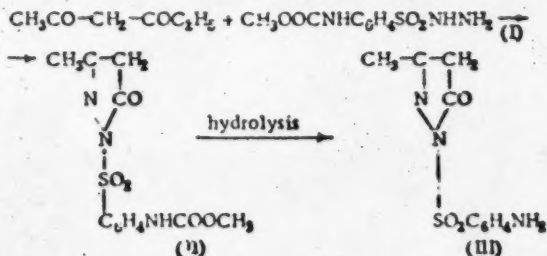
It would, for various reason, be of interest to investigate the analogous reaction with methyl *p*-aminobenzenesulfinate, and to prepare the metho-*p*-amino-benzenesulfonate of phenylmethylpyrazolone:



With this object we synthesized the carbomethoxy derivative of *p*-aminobenzenesulfonic acid, and prepared its methyl ester. However, a number of attempts at obtaining the product of addition of this ester to phenylmethylpyrazolone were unsuccessful, the ester always being recovered unchanged from the reaction. It is of interest that analogous experiments with methyl *p*-carbomethoxyaminobenzenesulfonate at once gave the expected addition product in good yield:

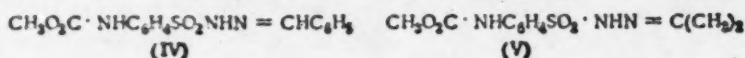


We next attempted to introduce the sulfamido group into the phenylmethylpyrazolone molecule in quite a different way. We know that a general method for preparing phenylmethylpyrazolone derivatives depends on condensation of phenylhydrazine with acetoacetic ester. Taking instead of hydrazine the hydrazide of *p*-carbomethoxyaminobenzene-sulfonic acid we hoped to obtain compound (III), of the desired structure:



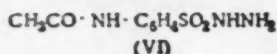
As the starting material for this reaction we synthesized the hydrazide of carbomethoxyaminobenzenesulfonic acid (I) in 81-82% yield, by the action of hydrazine hydrate on an ethereal solution of the chloroanhydride of N-carbomethoxysulfanilic acid. This compound reacts with acetoacetic ester in alcohol or dry toluene or xylene to give the corresponding hydrazone, with subsequent ring closure, affording N-carbomethoxy-p-aminophenyl-N-methylpyrazolonesulfone (II).

Numerous attempts at hydrolyzing the carbomethoxy derivative to give the free amino derivative (III) were unsuccessful, owing to the extreme stability of the bond between the carbomethoxy residue and the amino group; the products obtained by heating with acids or alkalis are either the initial product recovered unchanged, or else products of total breakdown of the pyrazolone ring. The carbomethoxy derivative of the hydrazide of p-aminobenzenesulfonic acid was similarly resistant to acid or alkaline hydrolysis. Further study of this compound showed that in general it reacts readily with substances containing the carbonyl group. This is illustrated in the experimental section of this paper by the condensation products with benzaldehyde (IV) or acetone (V):

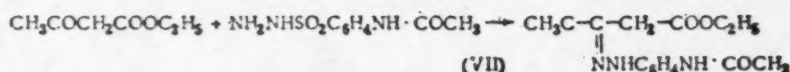


It is known that the acetyl group can usually be comparatively easily eliminated by hydrolysis, and we therefore decided to synthesize the hydrazide of N-acetylsulfanilic acid, in order to condense it with acetoacetic ester, so as to obtain compound (III).

The hydrazide (VI) of p-acetamidobenzenesulfonic acid was obtained in good yield (92-93%) by the action of hydrazine hydrate on the chloroanhydride of p-acetamidobenzenesulfonic acid:

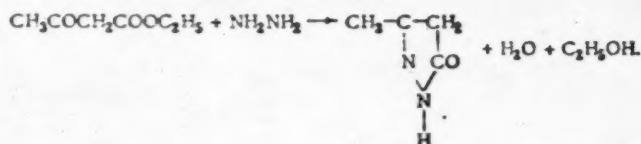


Condensation of this compound with acetoacetic ester gave only the corresponding hydrazone (VII) of acetoacetic ester, the second stage of the process, viz., elimination of alcohol with formation of the pyrazolone ring, not taking place:

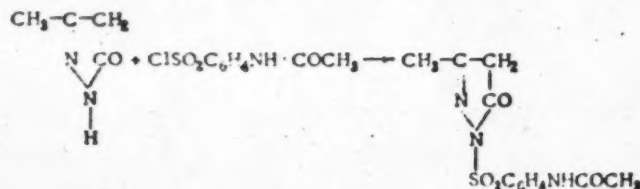


Unsuccessful attempts were made to synthesize the pyrazolone derivative by heating the hydrazone, either alone, or with various compounds able to combine with the alcohol liberated during ring closure; in all cases we either recovered the hydrazone unchanged, or else the products were uncrystallizable oils, attempts at fractional vacuum distillation of which led to production of a tarry mass.

These unsuccessful experiments obliged us to seek for other ways of synthesizing p-aminophenylmethylpyrazolonesulfone (III). The starting material was 3-methylpyrazolone, which was taken for condensation with the chloroanhydride of p-acetamidobenzenesulfonic acid. Methylpyrazolone was prepared according to Knorr [2], by reaction of acetoacetic ester with hydrazine hydrate:



The reaction proceeds smoothly in aqueous solution, and pure methylpyrazolone is obtained in one step, in ~80% yield. The product was condensed with the chloroanhydride of p-acetamidobenzenesulfonic acid, the best results being obtained in glacial acetic acid solution, in presence of anhydrous sodium acetate, when yields of ~65% of the acetyl derivative of the desired pyrazolone derivative were obtained:



Attempts at eliminating the acetyl group by hydrolysis showed that, similarly to the case of the carbomethoxy derivative, opening of the pyrazolone ring takes place very readily during hydrolysis. In this case, however, we found that when hydrolysis was conducted in acetone solution in presence of a small amount of hydrochloric acid the acetyl group is relatively readily eliminated, giving the free amino derivative in ~75% yield.

EXPERIMENTAL

Preparation of p-carbomethoxyaminobenzenesulfinic acid. $\text{CH}_3\text{OOCNH} \cdot \text{C}_6\text{H}_4\text{SO}_2\text{H}$

24.9 g of p-carbomethoxyaminobenzenesulfochloride (m.p. 108-110°) is added to 200 ml of a sodium sulfite solution obtained by mixing 50 ml of 36% aqueous NaHSO_3 with 150 ml of 5% aqueous sodium hydroxide, and the mixture is shaken for 2 hours, with occasional addition of caustic soda solution, so as to maintain an alkaline reaction (about 20 ml of 25% aq. NaOH). The mixture is then filtered, and the filtrate is made acid with 60% sulfuric acid, when the sulfinic acid separates as small colorless crystals, yield 19 g (83.7%), m.p. after one recrystallization from water 142-145°.

Found %: N 6.74.

$\text{C}_6\text{H}_7\text{O}_4\text{NS}$. Calculated %: N 6.51

Preparation of methyl p-carbomethoxyaminobenzenesulfinate through the silver salt of the sulfinic acid.

(a) Preparation of Ag salt. 15 g of p-carbomethoxyaminobenzenesulfinic acid is dissolved with heating in 148 ml of 2.5% aqueous sodium carbonate, and a solution of 11.8 g of silver nitrate in 150 ml of water is added to the hot solution, with vigorous stirring. The precipitate of Ag salt is drained on the filter-pump, and pressed on a porous tile, after which it is dried at 60°; yield 16 g (~71.5%).

Found %: Ag 33.41

$\text{C}_6\text{H}_7\text{O}_4\text{NSAg}$. Calculated %: Ag 33.51

(b) Preparation of methyl ester. 8.5 g (4 ml) of methyl iodide is added, with stirring, to 15.5 g of Ag salt in 100 ml of dry benzene, and the mixture is heated under reflux on the water bath for 2 hours. The hot solution is filtered, the residue of silver iodide is washed with a few portions of hot benzene, and the solvent is distilled off from the filtrate + washings. The residue melts at 173-182°, after recrystallization from methanol 182-183°; yield 7.3 g (66%).

Preparation of the methyl ester through the K salt of the sulfinic acid.

(a) Preparation of the K salt. A solution of 25 g of p-carbomethoxyaminobenzenesulfinic acid in 100 ml of 8% potassium carbonate is evaporated to dryness.

(b) Preparation of methyl ester. 10 g of methyl iodide is added gradually, with constant stirring, to 15 g of the K salt in 100 ml of methanol in a flask fitted with a reflux condenser, and placed on the water bath. Heating is continued for a further 2.5 hours, the hot solution is filtered, the solvent is distilled off from the filtrate, and the residue is recrystallized from methanol; yield of ester, m.p. 181-183°, 7.2 g (~53%).

Found %: C 47.37; H 4.70; N 6.42.

$\text{C}_8\text{H}_{11}\text{O}_4\text{NS}$. Calculated %: C 47.16; H 4.80; N 6.11.

All attempts at adding on this ester to phenylmethylpyrazolone, using the ordinary methods, were unsuccessful.

Preparation of methyl p-carbomethoxyaminobenzenesulfonate $\text{CH}_3\text{OOCNH} \cdot \text{C}_6\text{H}_4\text{SO}_2\text{CH}_3$

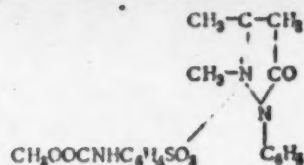
A solution of sodium methoxide prepared from 5 g of sodium and 150 ml of methanol is added gradually from a dropping funnel to a cooled (not more than 10°) and well stirred solution of 48 g of p-carbomethoxyaminobenzenesulfochloride in 200 ml of methanol, cooling is continued for 2 hours, and the precipitate is collected and dried; yield of ester 38 g (80.5%), m.p. after one recrystallization from methanol 115-116°.

Found %: N 5.39

$\text{C}_8\text{H}_{11}\text{O}_5\text{NS}$. Calculated %: N 5.71

Substitution of 30% caustic soda for sodium methoxide gave lower yields of ester (60-65%).

Preparation of the addition product of the ester to phenylmethylpyrazolone

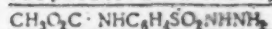


4.5 g of methyl *p*-carbomethoxybenzenesulfonate was heated with 3.5 g of phenylmethylpyrazolone for 30 minutes on an oil bath at 160°. The product was dissolved in water, and the solution was extracted with ether. The aqueous layer was evaporated to dryness on a water bath, and the residue was dissolved in ethanol. Addition of ether to the alcohol solution gave a white oily precipitate, which gradually crystallized, m.p. 58-60°.

Found %: C 52.86; H 5.42; N 9.37
 $\text{C}_{19}\text{H}_{21}\text{O}_6\text{N}_3\text{S}$. Calculated %: C 54.4; H 5.2; N 10.02.

The product does not appear to be sufficiently pure, but there can be no doubt as to its structure.

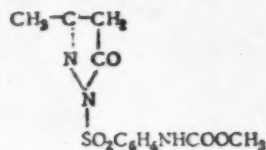
Preparation of the hydrazide of *p*-carbomethoxyaminobenzenesulfonic acid.



100 g of sodium bicarbonate is added to a solution of 25 g of *p*-carbomethoxyaminobenzenesulfochloride in 250 ml of ether, followed by a solution of 5 g of hydrazine hydrate in 45 ml of ethanol, added from a dropping funnel, with vigorous stirring and cooling (10-15°). Stirring is continued for a further 2 hours, and the mixture is then left overnight. The precipitate is then collected, washed with ether, and then with soda solution, and dried at 45-50°; yield of hydrazide 19.9 g (81%), m.p. 170-173°, rising to 181-188° (decomposition) after recrystallization from alcohol.

Found %: C 39.12; 38.97; H 4.53; 4.59; N 16.84; 16.67
 $\text{C}_8\text{H}_{11}\text{O}_4\text{N}_3\text{S}$. Calculated %: C 39.18; H 4.59; N 17.14

Preparation of *p*-carbomethoxyaminophenyl-N-3-methylpyrazolonesulfone

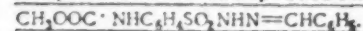


(a) 4.9 g of the hydrazide of *p*-carbomethoxyaminobenzenesulfonic acid is heated for 1 hour on the water bath with 3 ml of acetoacetic ester in 30 ml of alcohol, and the residue is recrystallized from 50 ml of alcohol, giving a product of m.p. 148-150°, raised to 156-158° by a second recrystallization from alcohol; yield 5 g (80.5% calculated on hydrazide taken).

(b) 4.9 g of hydrazide and 2.6 g of acetoacetic ester are mixed with 200 ml of dry toluene, and the solvent is distilled off, together with alcohol and water formed during condensation. The residue is recrystallized from alcohol, giving 5.6 g (90% yield, calculated on hydrazide) of product, m.p. 158-160°. Substitution of dry xylene for toluene lowered the yield to 70%.

Found %: N 13.63; 13.50
 $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}_3\text{S}$. Calculated %: N 13.50

Preparation of the *p*-carbomethoxyaminophenylsulfonylhydrazone of benzaldehyde



4 ml of benzaldehyde is added to a hot solution of 10 g of the hydrazide of *p*-carbomethoxyaminobenzenesulfonic acid in 100 ml of alcohol, and the mixture is boiled under reflux for 1 hour. 8.8 g of the hydrazone crystallized from the cooled solution, m.p. 198-200°, yield about 64.7%.

Found %: C 54.77; 54.81; H 4.68; 4.70; N 12.98; 12.95
 $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3\text{S}$. Calculated %: C 54.05; H 4.50; N 12.61

Preparation of the p-carbomethoxyaminophenylsulfonylhydrazone of acetone.
 $\text{CH}_3\text{COOC} \cdot \text{NHC}_6\text{H}_4\text{SO}_2\text{NNH}=\text{C}(\text{CH}_3)_2$

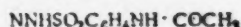
10 ml of acetone is added to a solution of 10 g of the hydrazide in 100 ml of glacial acetic acid at 50°, the solution is heated under reflux for 1 hour, and 59 ml of acetic acid is distilled off. 5 g of hydrazone crystallizes out from the cooled residue, m.p., after recrystallization from alcohol, 200-202°, yield 43%, calculated on hydrazide taken.

Found %: C 46.03; 46.15; H 5.24; 5.30; N 14.70; 14.86
 $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}_2\text{S}$. Calculated %: C 46.31; H 5.26; N 14.73.

Preparation of the hydrazide of p-acetamidobenzenesulfonic acid. $\text{CH}_3\text{CONHC}_6\text{H}_4\text{SO}_2\text{NNH}_2$

16 g of sodium bicarbonate is added to a solution of 20 g of p-acetamidobenzenesulfochloride in 400 ml of ether, followed by gradual addition of a solution of 20 g of hydrazine hydrate in 30 ml of methanol, with vigorous stirring. The mixture is left for 5 hours, and the precipitate is then collected, washed with ether and then with soda solution, and recrystallized from alcohol; yield of hydrazide 18.75 g, or 95.5%, calculated on acetamidobenzenesulfochloride taken.

Preparation of the hydrazone of acetoacetic ester derived from the hydrazide of p-acetamidobenzenesulfonic acid. $\text{CH}_3\text{C}-\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$



The solvent is distilled off from a solution of 3 g of the hydrazide and 1.7 ml of acetoacetic ester in 200 ml of dry benzene, and the residue is recrystallized from alcohol, giving the hydrazone, m.p. 118-120°, in 69% yield, calculated on hydrazide taken.

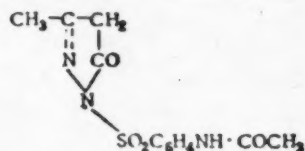
Found %: C 48.92; 49.03; H 6.00; 5.89; N 12.10; 12.21
 $\text{C}_{19}\text{H}_{19}\text{O}_5\text{N}_3\text{S}$. Calculated %: C 49.12; H 5.84; N 12.28

Preparation of methylpyrazolone $\text{CH}_3-\text{C}-\text{CH}_3$



A solution of 27 ml of hydrazine hydrate in 135 ml of water is added drop by drop, with vigorous stirring, to a suspension of 65 g of acetoacetic ester in 130 ml of water, and the mixture is then heated on the water bath for 30 minutes under reflux. The cooled solution deposits methylpyrazolone, in large colorless crystals, m.p. 210-213°, yield 38 g (77.5%).

Preparation of p-acetamidophenyl-N-methylpyrazolonesulfone



The yield of this reaction varies considerably according to the solvent taken. The reagents were taken in equimolecular amounts in all cases, and were heated: (a) in pyridine, (b) in acetone, (c) in glacial acetic acid; the respective yields were 30, 42 and 64%. We shall here describe only the third case:

18.6 g of p-acetamidobenzenesulfochloride, 7.85 g of methylpyrazolone, 8 g of anhydrous sodium acetate and 100 ml of glacial acetic acid were heated under reflux for 2 hours, after which 200 ml of cold water were added to the clear solution. The crystalline product which separates is recrystallized from 50% alcohol; yield 15.3 g, or 61.2% of theory, calculated on methylpyrazolone taken.

Found %: C 48.54; 48.45; H 4.88; 4.91; N 14.24; 14.13
 $\text{C}_{12}\text{H}_{13}\text{O}_4\text{N}_2\text{S}$. Calculated %: C 48.81; H 4.41; N 14.23

Hydrolysis of the acetyl derivative of pyrazolone.

Hydrolysis with dilute hydrochloric acid at low temperatures (75-80°) leads to opening of the pyrazolone ring, with production of sulfamic acid, which separates from the cooled reaction mixture. The hydrolysis may

however, be effected smoothly in acetone solution in the presence of a small amount of hydrochloric acid. 3 g of acetyl derivative is heated for 1 hour on the water bath under reflux with 3 ml of 35% hydrochloric acid in 30 ml of acetone, the acetone is distilled off, and the residue is made alkaline with ammonia, and extracted with chloroform. The extract gives 1.9 g of residue, a yield of 74%; the product melts at 152-155°, after recrystallization from 50% alcohol.

Found %: C 47.05; 46.96; H 4.90; 4.80; N 17.16; 17.11
 $C_{10}H_{11}O_3N_2S$. Calculated %: C 47.43; H 4.34; N 16.66

SUMMARY

1. The synthesis of p-carbomethoxyaminobenzenesulfonic acid and of its methyl ester are described.
2. It was found that an adduct of this ester with phenylmethylpyrazolone could not be prepared, whereas methyl p-carbomethoxyaminobenzenesulfonate readily adds on to it.
3. The hydrazide of p-carbomethoxyaminobenzenesulfonic acid has been synthesized, and has been shown to function as a reagent for compounds containing the carbonyl group.
4. Condensation of the hydrazide of p-carbomethoxyaminobenzenesulfonic acid with acetoacetic ester gives p-carbomethoxyaminophenyl-N-methylpyrazolonesulfone.
5. Hydrolysis of the carbomethoxy derivative to the free amine does not take place in acid or alkaline solution. Heating either gives no effect, or involves opening of the pyrazolone ring.
6. The hydrazide of N-acetylsulfanilic acid reacts with acetoacetic ester to give only the corresponding hydrazone; the second stage of the reaction, involving formation of the pyrazolone ring, does not take place.
7. p-Acetamidophenyl-N-methylpyrazolonesulfone is prepared by condensing methylpyrazolone with p-acetamidobenzenesulfochloride.
8. Hydrolysis of the acetyl group of this sulfone does not take place under the ordinary conditions, but proceeds smoothly when it is heated with a small amount of hydrochloric acid in acetone solution.

LITERATURE CITED

- [1] V.M. Rodionov, Bull. (4), 305 (1926).
- [2] L. Knorr, Ber. 43, 2106 (1910).

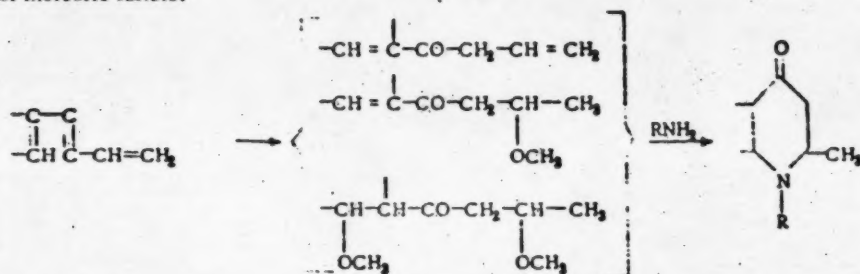
Received May 22, 1952.

ACETYLENE DERIVATIVES

PART 128. HETEROCYCLIC COMPOUNDS. XXIII. ACTION OF PRIMARY AROMATIC AMINES AND α -AMINOPYRIDINE ON VINYL ALLYL KETONES. SYNTHESIS OF ARYL-SUBSTITUTED γ -PIPERIDONES AND 1-(α -PYRIDYL)-4-PIPERIDONES

I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko

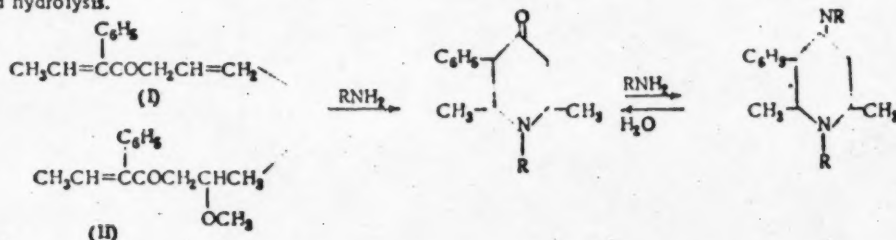
In 1948 a simple method was discovered in our laboratory for the synthesis of various 1-alkyl-4-piperidones [1], by the action of ammonia and primary alkylamines on vinyl allyl ketones and β -methoxy ketones, which are readily obtainable by the hydration of divinylacetylenic hydrocarbons in aqueous-methanol solution, in presence of mercuric sulfate:



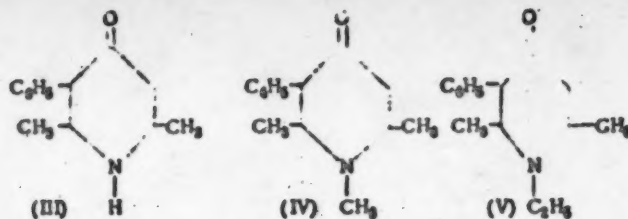
R = H or alkyl

The 4-piperidones are the basic intermediates for the synthesis of physiologically active compounds of the piperidone series, having, similarly to the naturally occurring alkaloids of the morphine and tropane groups, analgesic, anesthetic, spasmolytic, and midriatic action. Starting with 4-piperidones, we have in our laboratory synthesized numerous 4-piperidone derivatives, in particular various esters of 4-piperidols, in order to discover new physiologically active substances, and to elucidate the connection between their structure and their analgesic action [2]. In connection with these studies we thought it necessary to extend the area of application of the reaction of cyclization of vinyl allyl ketones with amines, on the one hand taking dienones with aromatic substituents, and on the other using aromatic amines. This would afford the possibility of achieving the synthesis of the little studied aryl-substituted γ -piperidones, in particular of those in which the aryl radical is substituted at the nitrogen atom.

As was expected, ammonia, methylamine, and ethylamine react with mixtures of 3-phenylhepta-2,6-dien-4-one (I) and methoxyketone (II) to give the corresponding 5-phenyl-4-piperidones, and, by further reaction between 4-piperidones and primary amines, 4-iminopiperines are formed, which readily regenerate the initial 4-piperidones by acid hydrolysis.

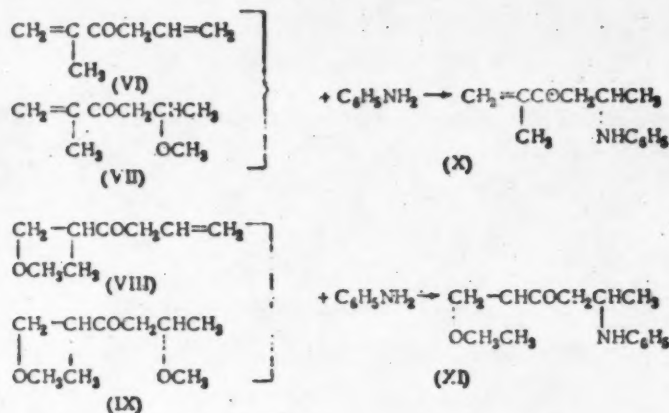


We thus synthesized 5-phenyl-2,6-dimethyl-4-piperidone (III) (yield 55%), 5-phenyl-1,2,6-trimethyl-4-piperidone (IV) (yield 50%), and 5-phenyl-2,6-dimethyl-1-ethyl-4-piperidone (V) (isolated as the picrate); these are the first described members of the series of 5-aryl substituted 4-piperidones:

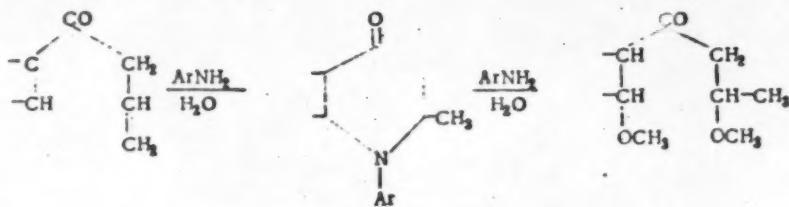


We next investigated the possibility of cyclization of vinyl allyl ketones with primary aromatic amines. We found that vinyl allyl ketones and their corresponding methoxyketones react in non-aqueous media with aromatic, as opposed to aliphatic, amines to give only addition products, which, similarly to other α,β -keto-arylamines, readily decompose when distilled.

Condensation of aniline with allyl isopropenyl ketone (VI) or with the methoxyketones (VII), (VIII), and (IX) gave β -anilinopropyl isopropenyl ketone (X) or β -anilinopropyl- β' -methoxyisopropyl ketone (XI), isolated as the picrates:

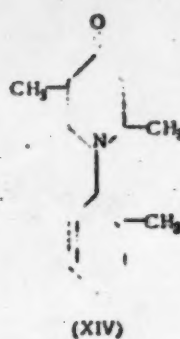
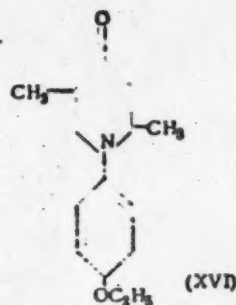
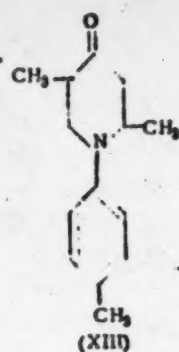
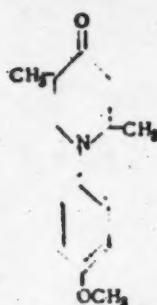
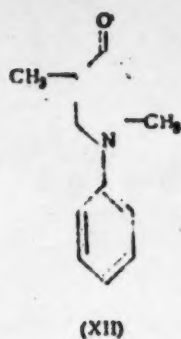


A detailed study of the conditions under which these reactions proceed showed that cyclization of vinyl allyl ketones and of their corresponding β -methoxyketones with arylamines proceeds readily in presence of water, according to the following general scheme:

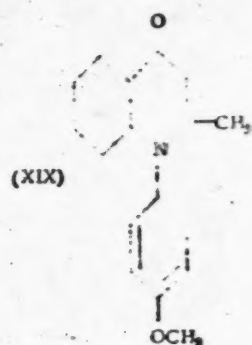
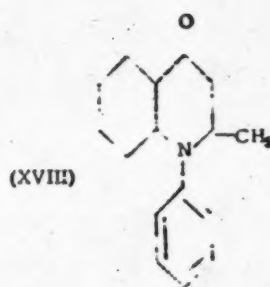
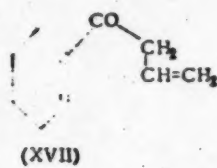


Addition products are, however, also found among the reaction products. The cyclization products were purified and isolated through the corresponding hydrochlorides.

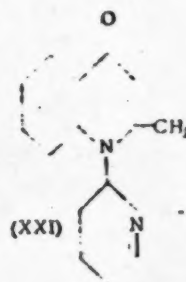
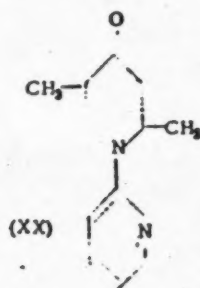
In this way, condensation of allyl isopropenyl ketone (VI), and of the methoxyketones (VII), (VIII) and (IX) with arylamines gave the following 1-aryl-4-piperidones: 1-phenyl-2,5-dimethyl-4-piperidone (XII), yield 45-50%, 1-*p*-tolyl-2,5-dimethyl-4-piperidone (XIII), yield 25%, 1-*o*-tolyl-2,5-dimethyl-4-piperidone (XIV), yield 30%, 1-*p*-methoxyphenyl-2,5-dimethyl-4-piperidone (XV), yield 58%, and 1-*p*-ethoxyphenyl-2,5-dimethyl-4-piperidone (XVI), yield 61%.



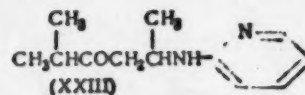
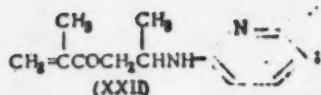
Condensation in presence of water of allyl Δ^1 -cyclohexenyl ketone (XVII) with aniline or *p*-anisidine gave 1-phenyl-2-methyl-4-ketodecahydroquinoline (XVIII) and 1-*p*-methoxyphenyl-4-ketodecahydroquinoline (XIX), in ~40% yield:



Condensation of α -aminopyridine with allyl isopropenyl ketone (VI) or allyl Δ^1 -cyclohexenyl ketone (XVII) in presence of water gave ~30% yields of 1- α -pyridyl-2,5-dimethyl-4-piperidone (XX) and 1- α -pyridyl-2-methyl-4-ketodecahydroquinoline (XXI), belonging to the interesting group of bisheterocyclic systems:



Under anhydrous conditions allyl isopropenyl ketone (VI) gives only the adduct (XXII), hydrogenation of which (Pd catalyst) gives the pyridylaminoketone (XXIII).



As appears from the Table below, in the cyclization of vinyl isopropenyl ketone with arylamines the basic factor determining the direction of the reaction and the yield of cyclization products is the basicity of the given aromatic amine. The yield of γ -piperidone rises parallel with increase in the basicity (dissociation constant) of the amine.

Serial No.	Amine	Dissociation constant	% Yield of piperidone
1	p-Toluidine	$2 \cdot 10^{-10}$	25
2	o-Toluidine	$3.4 \cdot 10^{-10}$	30
3	Aniline	$5 \cdot 10^{-10}$	45-60
4	p-Anisidine	$1.5 \cdot 10^{-9}$	58
5	p-Phenetidine	$2.15 \cdot 10^{-9}$	61

The highest yield of piperidone was obtained with allyl isopropenyl ketone and p-phenetidine, which is the most basic ($2.15 \cdot 10^{-9}$) of the amines taken.

The aryl-substituted 4-piperidones obtained by us are all stable liquid or crystalline compounds, which can be distilled in vacuo without decomposition, and which readily give derivatives, at either the nitrogen atom or the carbonyl group.

EXPERIMENTAL

5-Phenyl-2,6-dimethyl-4-piperidone (III)

14 g of a mixture of 3-phenylhepta-2,6-dien-4-one (I) and methoxyketone (II) (b.p. 95-115° [1 mm, n_D^{20} 1.5320 [3]) were added to 23.2 ml of aqueous ammonia (d 0.93) and 45 ml of methanol, and the mixture was heated in a steel cylinder on a water-bath at 60-70° for 4 hours. The ammonia and methanol were then removed by vacuum evaporation, initially at room temperature, and later on a water-bath at 45°. The residue was made neutral with 1:3 hydrochloric acid, and the neutral solution was exhaustively extracted with ether. The aqueous solution of salts of amines was treated with excess of solid alkali, and the brown oil separating was extracted with ether. The ethereal solution was dried with ignited potash, the ether was removed, and the dark-colored residue, which had partly crystallized, was vacuum distilled, giving 9 g of readily crystallizing product, b.p. 112° at 0.17 mm, m.p. 105-108°. Recrystallization from 50% alcohol gave 7.1 g of pure 5-phenyl-2,6-dimethyl-4-piperidone (III), colorless crystals, m.p. 108-109°.

Found %: N 6.82; 6.74

$\text{C}_{13}\text{H}_{17}\text{ON}$. Calculated %: N 6.88

Hydrochloride of 5-phenyl-2,6-dimethyl-4-piperidone. This was prepared by the action of hydrogen chloride on a solution of the base in absolute ether. After precipitation by absolute ether from alcohol it melted at 208-209° (decomposition).

Found %: N 5.61; 5.70

$\text{C}_{13}\text{H}_{17}\text{ONCl}$. Calculated %: N 5.84

The hydrochloride of the 2,4-dinitrophenylhydrazone was prepared by mixing alcoholic solutions of 5-phenyl-2,6-dimethyl-4-piperidone and 2,4-dinitrophenylhydrazine as yellow crystals (from methanol) m.p. 237-238° (decomposition).

The picrate of 5-phenyl-2,6-dimethyl-4-piperidone melted at 192-193° (from alcohol).

5-Phenyl-1,2,6-trimethyl-4-piperidone (IV)

12 ml of 34% aqueous methylamine and 50 ml of methanol were added to 10 g of a mixture of 3-phenylhepta-

2,6-dien-4-one (I), and the solution was heated for 8 hrs in a sealed tube on a water bath at 70°. The product was subjected to the usual treatment. Excess methylamine was removed in vacuum, the residue was made neutral with dilute hydrochloric acid, neutral products were extracted with ether, the free base was liberated by adding potash, extracted with ether, and the extract was dried with magnesium sulfate. The ether was distilled off, and the residue was vacuum distilled, giving 6.2 g of liquid, b.p. 120-129° at 1 mm, n_D^{20} 1.5446, which has an unpleasant odor, and rapidly darkens on exposure to the air.

In order to free the base of admixture of imino-derivative it was dissolved in 10% hydrochloric acid, and the solution was heated on a boiling water-bath for 4 hrs. The free base was then liberated by adding sodium hydroxide, extracted with ether, the solution was dried with magnesium sulfate, the ether was distilled off, and the residue was vacuum distilled, giving 4.5 g of pure 5-phenyl-1,2,6-trimethyl-4-piperidone (IV), b.p. 119-121° at 1 mm, n_D^{20} 1.5420; d_4^{20} 1.0515; found MR_D 65.22; calculated MR_D 65.60.

Found %: C 77.87; 77.81; H 8.77; 8.72.

$C_{16}H_{19}ON$. Calculated %: C 77.48; H 8.75

The picrate of 5-phenyl-1,2,6-trimethyl-4-piperidone melts at 140-141° (from alcohol-acetone mixture).

Found %: N 12.66; 12.47

$C_{20}H_{23}O_3N_4$. Calculated %: N 12.55

5-Phenyl-2,6-dimethyl-1-ethyl-4-piperidone (V)

10 g of a mixture of 3-phenylhepta-2,6-dien-4-one (I) with its corresponding methoxyketone (II) (b.p. 80-106° at 1 mm, n_D^{20} 1.551) and 10 ml of 50% aqueous ethylamine in 15 ml of methanol (for full dissolution of the ketones) were heated for 2 hrs in a sealed tube in a water-bath at 65-70°. The reaction product was treated in the same way as before, and vacuum distillation of the base obtained gave the following fractions:

Fraction I, b.p. 80-89° at 0.25 mm: n_D^{20} 1.5479; 1.7 g.

Fraction II, b.p. 90-100° at 0.2 mm: n_D^{20} 1.5475; 2.8 g.

Fraction III, b.p. 100-105° at 0.2 mm: n_D^{20} 1.5400; 0.8 g.

All the fractions had an unpleasant, mousy odor, due to the imino-ketone, and rapidly darken when exposed to the air. Addition to Fraction II of a saturated alcoholic solution of 3 g of picric acid gave a dark-colored precipitate of picrate, which after 2 recrystallizations from alcohol-acetone gave 2.7 g of the picrate of 5-phenyl-2,6-dimethyl-1-ethyl-4-piperidone (V), m.p. 150-151°.

Found %: N 11.85; 12.01

$C_{21}H_{24}O_3N_4$. Calculated %: N 12.16

1-Phenyl-2,5-dimethyl-4-piperidone (XII)

a) Action of aniline on allyl isopropenyl ketone (VI) in presence of water. 250 ml of dioxan was added to a boiling mixture (under reflux) of 110 g of allyl isopropenyl ketone (b.p. 48-50° at 12 mm, n_D^{20} 1.4691) [4], 93 g of freshly distilled aniline, and 60 ml of water, and the homogeneous solution was boiled for 23 hrs, during which time a liquid phase separated in increasing amount. The system was acidified with 1:1 hydrochloric acid, the dioxan and water were distilled off in vacuo, and the residue of salts of amines was dissolved in 200 ml of hot water. The cooled solution was extracted with ether, to remove neutral products, and it was then made alkaline with solid alkali. The dark-colored mass separating was extracted with ether, and the solution was dried with sodium sulfate, and fractionally distilled, giving the fractions:

Fraction I, b.p. 60-115° at 1 mm: 11.5 g

Fraction II, b.p. 115-130° at 1 mm: 150.7 g

Fraction III, b.p. 130-160° at 1 mm: 10.1 g (with decomposition)

Tarry residue - 22 g

Fraction II (b.p. 115-130° at 1 mm) was dissolved in 300 ml of 1:1 hydrochloric acid, and the solution was evaporated to dryness on a water-bath, in vacuo. The partly crystalline residue was treated with warm acetone, to purify the crystals of hydrochloride, which were then collected on the filter (145 g), washed with ether, and dissolved in water. Excess of alkali was added to the solution of hydrochloride, and the oil separating was again extracted with ether, the ethereal solution was dried with sodium sulfate, the ether was distilled off, and the residue was vacuum distilled, giving 102 g of 1-phenyl-2,5-dimethyl-4-piperidone (XII), a colorless, viscous oil,

insoluble in water, with a faint odor of aniline, b.p. 116-117° at 1 mm, n_D^{25} 1.5519, d_4^{25} 1.0650, experimental MR_D 60.98, calculated MR_D 60.55.

Found %: N 6.97; 6.91

$C_{13}H_{17}ON$. Calculated %: N 6.88

The hydrochloride of 1-phenyl-2,5-dimethyl-4-piperidone was prepared by passing dry hydrogen chloride through an ethereal solution of the base. It is readily soluble in water, but not in acetone. After recrystallization from alcohol-acetone mixture it melts at 157-157.5° (in a sealed capillary).

Found %: N 6.11; 5.88

$C_{13}H_{17}ONCl$. Calculated %: N 5.84

Found %: Cl 14.96

$C_{13}H_{17}ONCl$. Calculated %: Cl 14.80

The picrate of 1-phenyl-2,5-dimethyl-4-piperidone was prepared by mixing alcoholic solutions of picric acid and of the base; yellow crystals, insoluble in alcohol, m.p. 137-138°.

Found %: N 13.13; 12.95; 12.92

$C_{13}H_{17}O_8N_4$. Calculated %: N 12.96

The hydrochloride of the dinitrophenylhydrazone was prepared by adding an acid alcoholic solution of 2,4-dinitrophenylhydrazine to an alcoholic solution of 1-phenyl-2,5-dimethyl-4-piperidone; m.p. 183-183.5° (from alcohol).

Found %: N 16.48; 16.63

$C_{13}H_{17}N_5O_4Cl$. Calculated %: N 16.68

The acetone was distilled off from the filtrate from 1-phenyl-2,5-dimethyl-4-piperidone hydrochloride, and the dark, non-crystalline residue was dissolved in a small volume of water. The solution was alkalinized, the base separating was extracted with ether, and the extract was dried with sodium sulfate. Repeated fractional distillation in vacuo, which was associated with decomposition of the product, gave 6.5 g of base, b.p. 124-128° at 1 mm, a light yellow liquid with an odor resembling that of the initial dienone. Addition of a saturated alcoholic solution of picric acid (7 g) to an alcoholic solution of the base gave a yellow oil, from which a crystalline picrate was obtained by treatment with acetone-alcohol mixture. Fractional crystallization of the picrate from an ethanol-methyl ethyl ketone mixture gave 1.2 g of the picrate of β -anilinoisopropyl isopropenyl ketone (X), m.p. 125-126°.

Found %: N 13.1; 12.76

$C_{15}H_{21}O_8N_4$. Calculated %: N 12.96

b) Action of aniline on a mixture of methoxyketones (VII), (VIII), and (IX) in presence of water. 130 g of a mixture of the methoxyketones (VII), (VIII), and (IX) (b.p. 65-85° at 13 mm, n_D^{25} 1.4350) [4], 150 g of aniline, and 200 ml of water were heated to boiling under reflux, and 160 ml of methanol was added; the homogeneous solution was boiled for 22 hrs. The oily layer of base which separated from the cooled solution was dissolved by adding 200 ml of concentrated hydrochloric acid, and the acid solution was extracted with ether, to remove neutral products, and was then evaporated in vacuo. The semi-crystalline residue was repeatedly extracted with acetone, and the crystalline hydrochloride remaining was collected on the filter, and washed with ether.

The hydrochloride (125 g) was dissolved in water, and the solution was made alkaline. The oily layer separating was extracted with ether, dried with sodium sulfate, and vacuum distilled. Repeated distillation gave 82 g of the above-described 1-phenyl-2,5-dimethyl-4-piperidone (XII), b.p. 116-117° at 1 mm, n_D^{25} 1.5520, the picrate of which, m.p. 137.5-138°, gave no depression with the previous specimen.

c) Action of aniline on a mixture of the methoxyketones (VII), (VIII), and (IX), in absence of water. A mixture of 70 g of the methoxyketones (VII), (VIII), and (IX) (b.p. 65-85° at 13 mm, n_D^{25} 1.4350), 60 g of freshly distilled aniline, and 75 ml of anhydrous dioxan was boiled under reflux for 25 hrs, and the dioxan and unreacted reagents were distilled off in vacuo. Partial decomposition of the tarry residue (90 g) took place during its vacuum distillation. Repeated redistillation finally gave 11 g of product, b.p. 122-126° at 1 mm, n_D^{25} 1.5560.

An alcoholic solution of the product was left overnight with a saturated alcoholic solution of picric acid (12 g), giving 1.3 g of picrate, m.p. 137-139°, not giving any depression with the picrate of 1-phenyl-2,5-dimethyl-4-piperidone. The mother liquor, after removal of part of the solvent, gave 4.5 g of the picrate of β -anilinoisopropyl β -methoxyisopropyl ketone (XI), m.p. 104-105° (from alcohol).

Found %: N 12.14; 11.90
 $C_{14}H_{24}O_2N_2$ Calculated %: N 12.08

The base liberated from the picrate of m.p. 104-105° underwent decomposition when distilled; no individual products could be isolated from the distillate.

1-p-Tolyl-2,5-dimethyl-4-piperidone (XIII)

A solution of 93 g of a mixture of allyl isopropenyl ketone (VI) with the corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{25} 1.4281) in 200 ml of methanol was added gradually to a boiling emulsion of 100 g of p-toluidine (freshly distilled) in 300 ml of water, and boiling was continued under reflux for 24 hrs., after which 120 ml of concentrated hydrochloric acid was added to the cooled solution, which was then evaporated down under reduced pressure, and extracted with ether, to remove neutral products. The solution was saturated with solid caustic soda, the oil separating was twice extracted with ether, the ether solution was dried with sodium sulfate, the ether was distilled off, and the residue was fractionally distilled in vacuo. An ethereal solution of the fraction (56 g) boiling at 137-143° at 1.5 mm was saturated with hydrogen chloride, the hydrochloride which separated was collected, washed with acetone, and recrystallized from alcohol containing a small amount of water, giving 42 g of 1-p-tolyl-2,5-dimethyl-4-piperidone hydrochloride, glistening crystals, m.p. 158.5-160° (decomposition).

Found %: N 5.52; 5.58
 $C_{14}H_{23}ONCl$ Calculated %: N 5.52

Addition of aqueous potassium carbonate to an aqueous solution of the hydrochloride of m.p. 158.5-160° gave 1-p-tolyl-2,5-dimethyl-4-piperidone (XIII), b.p. 128° at 1 mm, n_D^{25} 1.5419; d_4^{25} 1.0420; found MR_D 65.5; calculated MR_D 65.17, a colorless, viscous liquid, which can be distilled without decomposition.

Found %: N 6.94; 6.81
 $C_{14}H_{19}ON$ Calculated %: N 6.45

1-o-Tolyl-2,5-dimethyl-4-piperidone (XIV)

A mixture of 95 g of allyl isopropenyl ketone (VI) with its corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{25} 1.4281), 100 g of freshly distilled o-toluidine, 300 ml of water, and 250 ml of methanol was boiled for 21 hrs. The methanol was then distilled off in vacuo, the solution was acidified with concentrated hydrochloric acid, and the solution was extracted with ether, to remove neutral products. The free base was liberated by adding solid alkali, and was extracted with ether, the ethereal solution was dried with sodium sulfate, the ether was distilled off, and the residue was vacuum distilled. An ethereal solution of the fraction boiling at 120-130° at 1 mm (67 g) was saturated with dry hydrogen chloride, the mixture of salts obtained was washed with acetone, and the residual material was recrystallized from 90% ethanol, giving 50.5 g of 1-o-tolyl-2,5-dimethyl-4-piperidone hydrochloride, m.p. 132.5-133.5°.

Found %: N 5.83; 5.79
 $C_{14}H_{23}ONCl$ Calculated %: N 5.52

Alkalization of an aqueous solution of the hydrochloride gave the free base 1-o-tolyl-2,5-dimethyl-4-piperidone (XIV), b.p. 107° at 0.5 mm, n_D^{25} 1.5288; d_4^{25} 1.0231; found MR_D 65.48; calculated MR_D 65.17, a colorless, viscous liquid, which can be distilled without decomposition.

Found %: N 6.87; 6.90
 $C_{14}H_{19}ON$ Calculated %: N 6.45

1-p-methoxyphenyl-2,5-dimethyl-4-piperidone (XV)

A mixture of 100 g of allyl isopropenyl ketone (VI) with its corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{25} 1.4281), 160 g of p-anisidine, 100 ml of water, and 170 ml of methanol was boiled under reflux for 25 hrs. The methanol was then distilled off in vacuo, the residue was made acid with 150 ml of concentrated hydrochloric acid, and the solution was extracted with ether to remove neutral products. The aqueous solution was evaporated to dryness in vacuo, and the residue was boiled for 2 hrs under reflux with 200 ml of acetone. The crystalline product was collected, washed with ether, and recrystallized from acetone containing a small amount of alcohol, giving 175 g of 1-p-methoxyphenyl-2,5-dimethyl-4-piperidone hydrochloride, m.p. 152.5-153.5°.

Found %: N 5.62; 5.50
 $C_{14}H_{21}O_2NCl$ Calculated %: N 5.20

Addition of aqueous ammonia to an aqueous solution of the hydrochloride (m.p. 152.5-153.5°) gave the free base 1-p-methoxyphenyl-2,5-dimethyl-4-piperidone (XV), colorless crystals (from light petroleum), m.p. 51.5-52.5°, b.p. 124-125° at 0.5 mm.

Found %: N 8.11; 6.31

$C_{14}H_{19}O_2N$. Calculated %: N 6.04

The hydrochloride of the dinitrophenylhydrazone was obtained by adding an alcoholic solution acidified with hydrochloric acid, of 2,4-dinitrophenylhydrazine to an alcoholic solution of 1-p-methoxyphenyl-2,5-dimethyl-4-piperidone; it melts at 188-188.5° (from alcohol).

Found %: N 15.46; 15.70

$C_{22}H_{24}O_6N_2Cl$. Calculated %: N 15.55

1-p-Ethoxyphenyl-2,5-dimethyl-4-piperidone (XVI)

A mixture of 35 g of allyl isopropenyl ketone (VI) with its corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{20} 1.4281), 35 g of p-phenetidine, 20 ml of water, and 20 ml of methanol was boiled under reflux for 21 hrs, and the dark, oily layer of base formed was separated, treated with 50 ml of concentrated hydrochloric acid, and extracted with ether, to remove neutral products. The aqueous layer was then cooled, when 9 g of phenetidine hydrochloride (m.p. 232-234°) separated. It was filtered off, and the filtrate was alkalinized with solid alkali, when an oil separated, which crystallized when cooled. It was collected, dried, and recrystallized from alcohol, giving 37 g of 1-p-ethoxyphenyl-2,5-dimethyl-4-piperidone (XVI), large crystals, m.p. 87-88°.

Found %: N 5.89; 6.07

$C_{15}H_{21}O_2N$. Calculated %: N 5.67

The hydrochloride of 1-p-ethoxyphenyl-2,5-dimethyl-4-piperidone was precipitated as an oil when an ethereal solution of the base was saturated with dry hydrogen chloride. The oil was dissolved in hot methyl ethyl ketone, and the cooled solution deposited the crystalline hydrochloride, m.p. 129-130°.

Found %: N 5.28; 5.25

$C_{15}H_{21}O_2NCl$. Calculated %: N 4.93

1- α -pyridyl-2,5-dimethyl-4-piperidone (XX)

a) Action of α -aminopyridine on a mixture of methoxyketones (VII), (VIII), and (IX). In presence of water.

A mixture of 100 g of methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{20} 1.4281), 100 g of α -aminopyridine, and 400 ml of water was boiled for 5 hrs, and the oily layer separating from the cooled solution was separated and vacuum distilled, giving 65 g of distillate boiling at 120-125° at 1 mm, a viscous liquid, darkening on exposure to the air, and possessing an unpleasant odor. The hydrochloride obtained by saturating an ethereal solution of the fraction with hydrogen chloride was extracted a few times with hot acetone, and was then twice precipitated from alcohol by means of ether, giving 55 g of monohydrochloride of 1- α -pyridyl-2,5-dimethyl-4-piperidone, m.p. 149-150°.

Found %: N 11.74; 11.90; Cl 14.48

$C_{13}H_{17}N_2OCl$. Calculated %: N 11.60; Cl 14.75

Alkalinization of an aqueous solution of the hydrochloride gave the free base 1- α -pyridyl-2,5-dimethyl-4-piperidone (XX), m.p. 70-71° (from light petroleum), b.p. 112° at 0.5 mm, small odorless crystals, insoluble in water.

Found %: N 13.60; 13.90

$C_{12}H_{15}N_2O$. Calculated %: N 13.72

b) Action of α -aminopyridine on allyl isopropenyl ketone (VI) in absence of water. A mixture of 15 g of allyl isopropenyl ketone (b.p. 43-46° at 11 mm, n_D^{20} 1.4705) and 12 g of α -aminopyridine (m.p. 57°) was heated for 20 min. on a boiling water-bath, and the mixture was then fractionally distilled in vacuum. The following fractions were obtained, after the unchanged reagents had been distilled off (6.8 g of allyl isopropenyl ketone and 4.4 g of α -aminopyridine):

Fraction I, b.p. 73-126° at 3 mm; 2.6 g

Fraction II, b.p. 127-129° at 3 mm; 8.2 g; n_D^{20} 1.5580.

Fraction I partly crystallized, and the crystals were found to be α -aminopyridine, m.p. 57°. Fraction II is a viscous, yellow liquid, with a sharp, unpleasant odor; it rapidly darkens on standing. Redistillation of Fraction II gave the fractions:

Fraction I, b.p. 45-49° at 11 mm, 1.0 g; n_D^{20} 1.4700
 Fraction II, b.p. 70-128° at 2.5 mm; 2.2 g;
 Fraction III, b.p. 129-131° at 2.5 mm; 2.5 g; n_D^{20} 1.5575

Fraction I is allyl isopropenyl ketone, and the crystals separating from Fraction II were found to be α -aminopyridine, m.p. 57°.

Thus the product of reaction of allyl isopropenyl ketone with α -aminopyridine, in absence of water, decomposes when vacuum distilled, regenerating the initial reagents: it is β -(α -aminopyridino)-propyl isopropenyl ketone (XXII), b.p. 129-131° at 2.5 mm, n_D^{20} 1.5575; d_4^{20} 1.0554; found MR_D 62.27; calculated MR_D 60.30, the picrate of which melts at ~230° (decomposition) (from alcohol).

The same product, β -(α -aminopyridino)-propyl isopropenyl ketone (XXII), is obtained when a mixture of methoxyketones (VII) and (VIII) is heated in absence of water. The theoretical amount of hydrogen was absorbed when 4.5 g of this product in 10 ml of alcohol was hydrogenated with Pd catalyst at room temperature. The alcohol was then distilled off, and the residue was twice distilled in vacuum, giving 1.3 g of β -(α -aminopyridino)-propyl isopropenyl ketone (XXII), a faint yellow liquid, b.p. 125-126° at 4 mm, n_D^{20} 1.5280; d_4^{20} 1.0243; found MR_D 61.98; calculated MR_D 60.77; picrate, m.p. 130-151° (from alcohol)

1-Phenyl-2-methyl-4-ketodecahydroquinoline (XVIII)

A mixture of 28 g of allyl Δ^1 -cyclohexenyl ketone (XVII) (b.p. 108° at 9 mm, n_D^{20} 1.5102) [5] 27 g aniline, 65 ml of water, and 120 ml of dioxan was boiled under reflux for 15 hrs, and the oily product separating after cooling was vacuum distilled, giving 27 g of a fraction, b.p. 140-146° at 1 mm, which crystallized on standing. Recrystallization from light petroleum gave 15.3 g of 1-phenyl-2-methyl-4-ketodecahydroquinoline (XVIII), large crystals, insoluble in water, m.p. 101-103°.

Found %: N 5.77; 5.97

$C_{18}H_{21}ON$. Calculated %: N 5.75

The hydrochloride of 1-phenyl-2-methyl-4-ketodecahydroquinoline was obtained by saturating an ethereal solution of the base with dry hydrogen chloride; after recrystallization from alcohol-ether mixture it had m.p. 142-143°.

Found %: N 5.17; 5.27

$C_{18}H_{21}ONCl$. Calculated %: N 5.00

1-p-Methoxyphenyl-2-methyl-4-ketodecahydroquinoline (XIX)

A mixture of 20 g of allyl Δ^1 -cyclohexenyl ketone (XVII) (b.p. 108° at 9 mm, n_D^{20} 1.5102), 18 g of p-anisidine, 13 ml of water, and 18 ml of methanol was boiled under reflux for 12 hrs, and the dark oil which separated on cooling was distilled in vacuum. The fraction (20g) of b.p. 145-160° at 1 mm was dissolved in ether, and the solution was saturated with dry hydrogen chloride. The mixture of salts so obtained was washed with acetone, and recrystallized from alcohol-methyl ethyl ketone mixture, giving 16.5 g of 1-p-methoxyphenyl-2-methyl-4-ketodecahydroquinoline hydrochloride, m.p. 150-151°.

Found %: N 4.83; 4.71

$C_{17}H_{24}O_2NCl$. Calculated %: N 4.52

Addition of aqueous ammonia to an aqueous solution of the hydrochloride gave colorless, odorless crystals of 1-p-methoxyphenyl-2-methyl-4-ketodecahydroquinoline (XIX), m.p. 98-99°, insoluble in water.

Found %: N 5.21; 5.25

$C_{17}H_{23}O_2N$. Calculated %: N 5.14

1- α -Pyridyl-2-methyl-4-ketodecahydroquinoline (XX)

A solution of 10 g of allyl Δ^1 -cyclohexenyl ketone (XVII) (b.p. 108° at 9 mm, n_D^{20} 1.5102), 16 ml of water, and 1.5 g of α -aminopyridine was boiled under reflux for 22 hrs, and the dark oil separating from the cooled solution was vacuum distilled. The fraction (6.1 g) boiling at 155-160° at 1 mm was dissolved in alcohol, and an alcoholic

solution of 6 g of picric acid was added. The product was recrystallized from alcohol-acetone mixture, giving 5.2 g of the monopicrate of 1- α -pyridyl-2-methyl-4-ketodecahydroquinoline (XXI), a yellow powder, m.p. 145-146°.

Found %: N 14.90; 14.85

$C_{21}H_{23}O_3N_3$. Calculated %: N 14.80

SUMMARY

1. New 5-phenyl-4-piperidones have been prepared by cyclization of 3-phenylhepta-2,6-dien-4-one with ammonia, methylamine, and ethylamine. In contrast to aliphatic amines, aromatic amines react with vinyl allyl ketones in absence of water to give only addition products. Cyclization of allyl isopropenyl ketone and allyl Δ^1 -cyclohexenyl ketone with primary aromatic amines or α -aminopyridine is effected in presence of water.
2. A general method is advanced for the preparation of 1-aryl-4-piperidones and 1- α -pyridyl-4-piperidones.
3. The yield of cyclization product is shown to be proportional to the basicity of the aromatic amine taken.

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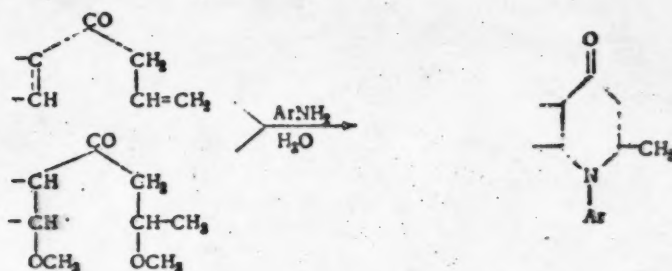
ACETYLENE DERIVATIVES

PART 129. HETEROCYCLIC COMPOUNDS

XXIV. TRANSFORMATIONS OF 1-PHENYL-2,5-DIMETHYL-4-PIPERIDONE

I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko

The preceding paper described the synthesis of 1-aryl-4-piperidones, which are readily formed by cyclization of vinyl allyl ketones or of their corresponding β -methoxyketones with primary aromatic amines, in presence of water [1]:



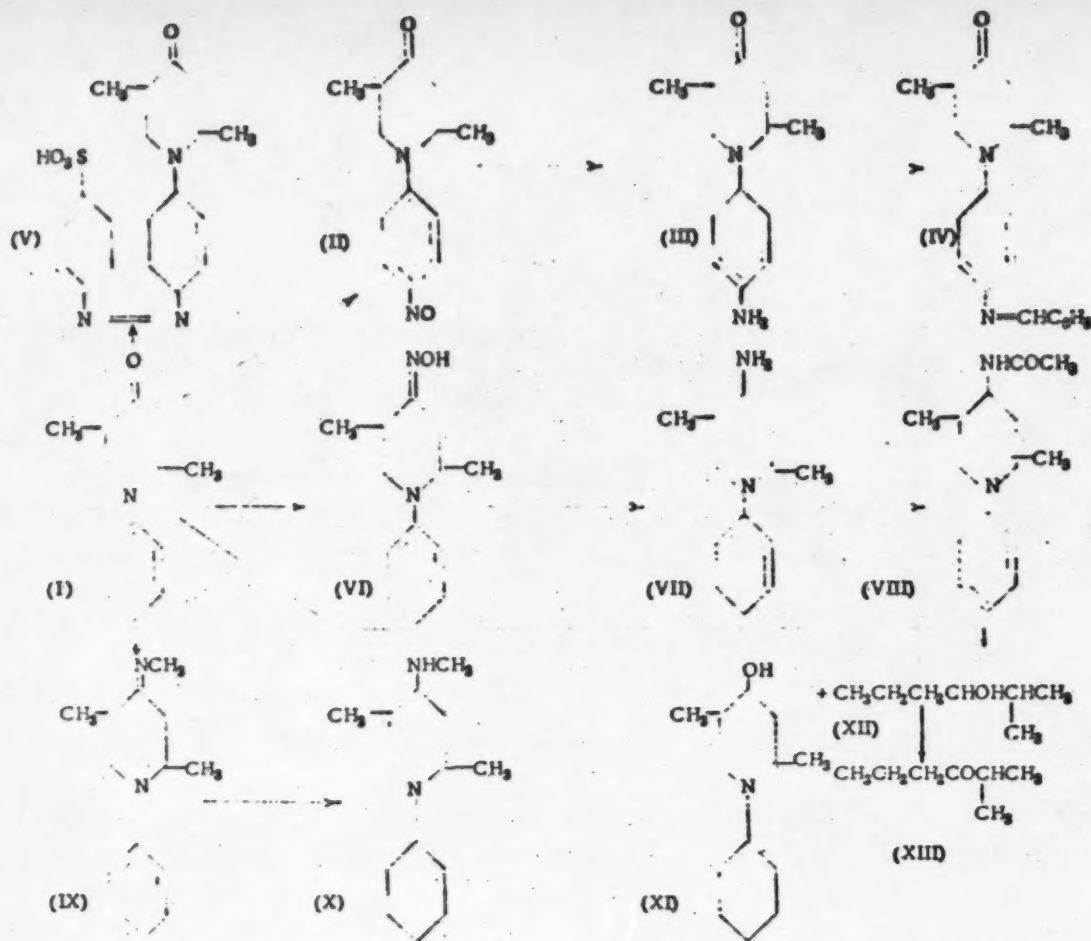
N-Aryl-4-piperidones have been little studied up till now, because of the difficulty of their preparation. The only known representatives of this group were 1-phenyl-4-piperidone (only the hydrochloride was described) [2] and 1,2,6-triphenyl-4-piperidone [3].

The simple and general method for synthesis of 1-aryl-4-piperidones described by us afforded us the opportunity of studying various reactions of 1-phenyl-2,5-dimethyl-4-piperidone (I), which is readily prepared from the commercially obtainable methylvinylethynylcarbinol and aniline. 1-Phenyl-2,5-dimethyl-4-piperidone (I), similarly to dialkylanilines, reacts in the cold with nitrous acid, giving 1-*p*-nitrosophenyl-2,5-dimethyl-4-piperidone (II) in 73% yield; green granules with a metallic sheen. This nitroso-compound is reduced by stannous chloride in hydrochloric acid solution to 1-*p*-aminophenyl-2,5-dimethyl-4-piperidone (III) (96% yield), which, in the same way as other aromatic amines, readily condenses with benzaldehyde, giving a 63% yield of the Schiff's base 1-*p*-benzylideneaminophenyl-2,5-dimethyl-4-piperidone (IV).

1-Phenyl-2,5-dimethyl-4-piperidone (I) readily couples with *p*-diazobenzenesulfonic acid, giving the azo-dye (V) in 66% yield. Its sodium salt resembles methyl orange in giving yellow aqueous solutions which change to an intense red when the solution is acidified.

Addition of hydroxylamine to an aqueous alcoholic solution of 1-phenyl-2,5-dimethyl-4-piperidone (I) gives a quantitative yield of the oxime (VI), as a mixture of stereoisomeric syn- and anti-isomers, which we were not able to separate by means of fractional crystallization. Reduction of oxime (VI) gave the expected 4-amino-1-phenyl-2,5-dimethylpiperidine (VII), which avidly absorbs atmospheric carbon dioxide, affording the carbonate. The primary amine (VII) (or its carbonate) is easily acetylated with acetic anhydride, giving 4-acetamido-1-phenyl-2,5-dimethylpiperidine (VIII).

Condensation of 1-phenyl-2,5-dimethyl-4-piperidone (I) with methylamine gives 4-methylimino-1-phenyl-2,5-dimethylpiperidine (IX), a liquid which darkens when exposed to the air, and which possesses the characteristic unpleasant odor of imines. Hydrogenation of this imine (Pd catalyst) affords 4-methylamino-1-phenyl-2,5-dimethylpiperidine (X): (see top of next page).



Exhaustive hydrogenation under pressure (200-250°; 90 atm), with Raney Ni catalyst, converts 1-phenyl-2,5-dimethyl-4-piperidone (I) into the known 1-cyclohexyl-2,5-dimethyl-4-piperidol (XI), together with products of opening of the piperidine ring. The low b.p. fraction, after elimination of basic compounds, was found to contain 2-methylhexan-3-ol (XII), identified as the semicarbazone of 2-methylhexan-3-one (XIII). It follows that the piperidine ring ruptures at the nitrogen atom.

EXPERIMENTAL

1-Phenyl-2,5-dimethyl-4-piperidone (I) was prepared by the method given in our preceding paper [1], by the cyclization of allyl isopropenyl ketone and its corresponding methoxyketones with aniline, in presence of water.

1-*p*-Nitrosophenyl-2,5-dimethyl-4-piperidone (II). 24 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 116-118° at 1 mm, n_D^{20} 1.5521) was dissolved in 98 ml of 1:1 hydrochloric acid, in a porcelain beaker. The beaker was cooled in ice, 50 g of ice was added to it, and a cooled solution of 9.5 g of sodium nitrite in 40 ml of water was added drop by drop, from a dropping funnel, with energetic shaking. The hydrochloride which separates after an hour was collected, and the filtrate was concentrated, when a further batch of hydrochloride crystallized out. After recrystallization from a mixture of concentrated hydrochloric acid and alcohol 23.2 g of 1-*p*-nitrosophenyl-2,5-dimethyl-4-piperidone hydrochloride was obtained; well-formed orange-yellow crystals, m.p. 152-153°.

The free base was obtained by shaking a mixture of the hydrochloride with ether and aqueous sodium carbonate, separating the emerald green ethereal layer, and evaporating off the solvent in a porcelain dish. The mixture was recrystallized from an alcohol-gasoline mixture, to give 1-*p*-nitrosophenyl-2,5-dimethyl-4-

piperidone (II), m.p. 130-130.5°, small green crystals with a metallic sheen.

Found %: N 11.97; 12.14

$C_{13}H_{15}O_2N_2$. Calculated %: N 12.03

1-p-Nitrosophenyl-2,5-dimethyl-4-piperidone is instantly hydrolyzed by aqueous alkalis, with production of p-nitrosophenol and 2,5-dimethyl-4-piperidone, which undergoes condensation under the conditions of the reaction. p-Nitrosophenol is identified by the Liberman reaction, after separation from the tarry products.

1-p-Aminophenyl-2,5-dimethyl-4-piperidone (III): A solution of 1-p-nitrosophenyl-2,5-dimethyl-4-piperidone hydrochloride, prepared as above from 18 g of 1-p-phenyl-2,5-dimethyl-4-piperidone, 75 ml of hydrochloric acid, and 7.5 g of sodium nitrite in 50 ml of water, was added drop by drop to a solution of 50 g of stannous chloride in 60 ml of concentrated hydrochloric acid, at 40-60° with constant stirring. After all the nitroso-compound had been added the flask was placed on a boiling water-bath, and stirring was continued for a further 50 min. The reaction mixture was then made alkaline with 50% caustic potash, and the dark-colored product was extracted with ether. The ether was then distilled off, and the residue was recrystallized from alcohol, giving 13.6 g of 1-p-amino-phenyl-2,5-dimethyl-4-piperidone (III) crystals, m.p. 135.5-136.5°, which rapidly darken on exposure to the atmosphere.

Found %: N 13.01; 13.03

$C_{13}H_{15}ON_2$. Calculated %: N 12.83

The hydrochloride of the dinitrophenylhydrazine was obtained by adding an alcoholic solution of 2,4-dinitrophenylhydrazine, acidified with hydrochloric acid, to an alcoholic solution of 1-p-aminophenyl-2,5-dimethyl-4-piperidone: it melts at 115-116°; after recrystallization from alcohol.

1-p-Benzylideneaminophenyl-2,5-dimethyl-4-piperidone (IV): A mixture of 2 g of 1-p-aminophenyl-2,5-dimethyl-4-piperidone (m.p. 135.5-136.5°), 5 ml of alcohol, and 2 ml of benzaldehyde was heated at 60-70° for 1 hour. The cooled solution deposited yellow crystals, recrystallization of which from absolute alcohol gave 1.9 g of 1-p-benzylideneaminophenyl-2,5-dimethyl-4-piperidone (IV), yellow crystals, m.p. 130.5-131.5°.

Found %: N 9.26; 9.32

$C_{21}H_{23}ON_2$. Calculated %: N 9.14

4-(2,5-dimethyl-4-ketopiperidino)-azobenzene-4'-sulfonic acid (V): A solution of 5 g of sodium sulfanilate and 2 g of sodium nitrite in 20 ml of water was added to a mixture of 12 ml of concentrated hydrochloric acid and 50 g of crushed ice, and the resulting solution of diazobenzenesulfonic acid was cooled to -4°, and added drop by drop, with stirring, to a solution of 5 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 116-118° at 1 mm; n_D^{20} 1.5521) in 6 ml of hydrochloric acid (1:1).

The solution was made alkaline with dilute caustic soda, when a brown precipitate of the azo-dye (V) separated. It was collected and washed on the filter with water; yield 6.5 g of sodium 4-(2,5-dimethyl-4-ketopiperidino)-azobenzene-4'-sulfonate (V), a brown powder, dilute solutions of which are colored yellow, changing to an intense red when acidified.

Found %: N 10.13; 10.35

$C_{13}H_{15}O_4N_2Na$. Calculated %: N 10.26

4-Amino-1-phenyl-2,5-dimethylpiperidine (VII): a) Preparation of the oxime of 1-phenyl-2,5-dimethyl-4-piperidone (VI). A solution of 30 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 117-118° at 1 mm; n_D^{20} 1.5519) in 150 ml of alcohol was mixed with a solution of 30 g of hydroxylamine hydrochloride and 60 g of sodium acetate in 100 ml of water, and the resulting suspension was heated for a short time on a water-bath. The cooled solution was filtered, and the residue was dried in a vacuum desiccator, giving 31 g of the oxime of 1-phenyl-2,5-dimethyl-4-piperidone (VI), which melted at 70-83° after two recrystallizations from 50% alcohol.

Found %: N 12.80; 13.14

$C_{13}H_{17}ON_2$. Calculated %: N 12.83

b) Reduction of the oxime of 1-phenyl-2,5-dimethyl-4-piperidone (VI). A solution of 25 g of oxime in 300 ml of isoamy¹ alcohol was placed in a flask fitted with a stirrer and a reflux condenser, and 24 g of sodium was added gradually, avoiding violent boiling of the system. The flask is then heated until all the sodium has dissolved, and the solution was then cooled, 250 ml of water and 400 ml of ether were added, the ethereal extract

was washed with 100 ml of water, and dried with sodium sulfate. The ether and the isoamyl alcohol were then distilled off, and the residue was vacuum distilled, giving 18 g of 4-amino-1-phenyl-2,5-dimethylpiperidine (VII), a colorless liquid with a powerful odor of amine, b.p. 114-115° at 1 mm, n_D^{20} 1.5425; d_4^{20} 1.0035; found MR_D 64.11; calculated MR_D 63.98.

Found %: N 13.78; 13.73

$C_{13}H_{19}N$. Calculated %: N 13.71

The amine thus obtained readily absorbs atmospheric carbon dioxide, giving a carbonate, m.p. above 100°.

4-Amino-1-phenyl-2,5-dimethylpiperidine dihydrochloride was obtained by passing dry hydrogen chloride into a solution of the amine in ether-alcohol mixture. It melted at 204-206°, after recrystallization from absolute alcohol.

Found %: Cl 25.11

$C_{13}H_{17}N_2Cl_2$. Calculated %: Cl 25.60

4-Acetamido-1-phenyl-2,5-dimethylpiperidine (VIII). 2 g of 4-amino-1-phenyl-2,5-dimethylpiperidine (b.p. 114-115° at 1 mm, n_D^{20} 1.5425) was mixed with 2.5 g of acetic anhydride, and the mixture was heated on the water-bath for 30 min., after which it was made alkaline with 20% potassium hydroxide solution. The crystalline precipitate was washed with water; yield, 2.2 g of 4-acetamido-1-phenyl-2,5-dimethylpiperidine (VIII), m.p. 146-148° (from alcohol-gasoline mixture).

Found %: N 11.33; 11.26

$C_{15}H_{21}ON_2$. Calculated %: N 11.37

4-Methylamino-1-phenyl-2,5-dimethylpiperidine (X). 9 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 116-118° at 1 mm, n_D^{20} 1.5519) was placed in a glass tube immersed in a freezing mixture, and dry methylamine was passed until the weight had increased by 11.5 g, when the tube was sealed and heated for 3 hrs at 65°. The excess of methylamine was removed under reduced pressure, and the residue was dissolved in 30 ml of absolute alcohol. The solution of 4-methylamino-1-phenyl-2,5-dimethylpiperidine (IX) was hydrogenated (Pt catalyst; Adams method): 730 ml of hydrogen (19° at 758 mm). 6.5 g of a colorless, viscous liquid with a characteristic odor of amine was obtained, b.p. 119-121° at 1 mm, n_D^{20} 1.5522, and its ethereal solution was saturated with dry hydrogen chloride, giving a colorless hygroscopic hydrochloride, which was purified by dissolving in acetone and precipitating out with ether, giving 3.1 g of 4-methylamino-1-phenyl-2,5-dimethylpiperidine dihydrochloride (X), m.p. 195.5-197° (in a sealed capillary), as small crystals, readily soluble in water.

Found %: N 9.39; 9.51; 9.32; Cl 24.06

$C_{14}H_{20}N_2Cl_2$. Calculated %: N 9.61; Cl 24.37

1-Cyclohexyl-2,5-dimethyl-4-piperidol (XD). 46 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 115-116° at 0.8 mm, n_D^{20} 1.5521) in 53 ml of alcohol was hydrogenated (0.6 g of Raney Ni) in a rotating autoclave of capacity 156 ml, at 200-250° and an initial hydrogen pressure of 90 atm. Altogether 4.33 moles of hydrogen were absorbed per mole of piperidone. The solution was filtered, to remove catalyst, and the hydrogenation product was fractionally distilled in vacuum, giving the following fractions:

Fraction I, b.p. 70-100° at 10 mm; 24 g

Fraction II, b.p. 115-125° at 1 mm; 13 g

An ethereal solution of Fraction II (b.p. 115-125° at 1 mm) was saturated with hydrogen chloride, to give a hydrochloride which, after two recrystallizations from alcohol, melted at 305-307°, and which when treated with 25% aqueous ammonia yielded the free base, m.p. 85-86° (from gasoline). The base and its hydrochloride gave no m.p. depression when mixed with 1-cyclohexyl-2,5-dimethyl-4-piperidol (XD) or its hydrochloride, previously prepared in our laboratory from 2,5-dimethyl-4-piperidone (m.p. 98°), formic acid, and cyclohexanone.

An ethereal solution of Fraction I (b.p. 70-100° at 10 mm) was saturated with hydrogen chloride, and the ethereal layer was carefully decanted off. The residue after the ether had been distilled off, consisting of neutral products, was three times distilled at atmospheric pressure, giving 2.1 g of substance of b.p. 140-143°, n_D^{20} 1.4190 (the literature [4] gives for 2-methylhexan-3-ol (XII) a b.p. of 141-142°, n_D 1.41493). The product (1.5 g) was shaken for 1 hr with a solution of 1.2 g of potassium dichromate in 30% sulfuric acid, and the oxidation product was extracted with ether. Its semicarbazone melted at 116-118° (from 50% alcohol), and gave no depression

of m.p. with the semicarbazone, m.p. 117-119°, of a known sample of 2-methyl-hexan-3-one (XIII) [5].

SUMMARY

A series of transformations of 1-phenyl-2,5-dimethyl-4-piperidone (I) affecting the keto group and the phenyl radical are described. The compounds II - XI have not previously been described.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

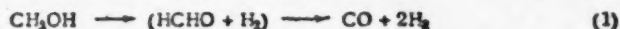
PART 9. REACTION OF METHANOL AND ETHANOL WITH ETHYLENE

Ya. T. Eldus and I. V. Guseva

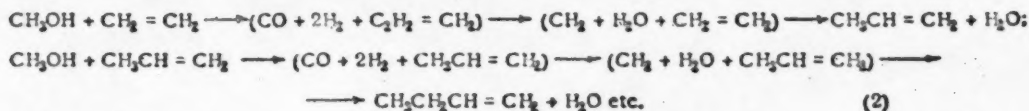
It has been shown earlier [1,2,3] that a mixture of ethylene and hydrogen does not react under the ordinary conditions of catalytic hydrocondensation unless the mixture contains some carbon monoxide, even very small admixtures being effective in this respect. The effect increases as the carbon monoxide content of the mixture rises from 0 to 6%, as is shown by rise in the yield of hydrocarbons, in particular of the heavier fractions. It was suggested that the methylene radicals formed at the catalyst surface by hydrogenation of carbon monoxide may act as initiators of the reaction, and may at the same time enter into the composition of the newly formed hydrocarbon molecules, as is shown by the presence among the reaction products of hydrocarbons with an odd number of carbon atoms in the molecule.

It was natural to expect that the same condensing action on ethylene (olefin) hydrogen mixtures would be exerted by such substances which would not under the given conditions act as contact catalyst poisons, but would decompose to yield either methylene radicals (for example, ketene [4] or perhaps diazomethane) or carbon monoxide, which could undergo hydrogenation at the catalyst surface to yield methylene radicals.

We first examined methanol as being a substance whose chemical structure is such as would lead us to expect it to exert a condensing effect in the reaction with ethylene, since it is known that methanol readily decomposes at various contact catalysts with liberation of carbon monoxide, by the reaction:



Moreover, since the second product of reaction (1) is hydrogen, the presence of which is necessary for the reaction of hydrocondensation of carbon monoxide with olefins, it could have been supposed that it would under the given conditions be possible [1,2] to realize the reaction of hydrocondensation of methanol with the simpler olefins, according to the scheme:

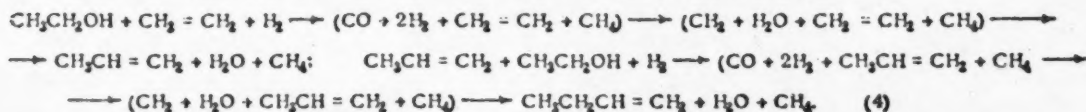


The same reasoning would apply to ethanol, under such conditions [5] of catalyzed decomposition as in the reaction:



i.e., with formation of carbon monoxide and hydrogen.

Hydrocondensation of ethylene with ethanol would accordingly proceed as follows:



The results of the present research do in fact show that both methanol and ethanol exert a condensing effect on ethylene-hydrogen mixtures, as well as entering into reaction with ethylene to yield final reaction products. In view of the common features of the mechanism of hydrocondensation of carbon monoxide with ethylene and of methanol or ethanol with ethylene, we must accept the intermediate formation from the alcohols of carbon monoxide and hydrogen, and subsequently of methylene radicals, i.e., we must admit the correctness of the reaction schemes (3) and (4).

EXPERIMENTAL

The apparatus, the preparation and analysis of the initial and final gases, and the experimental methods applied, were the same as in our earlier papers [1,2]. The methanol used boiled at 64.4-64.6° at 755 mm, d_4^{20} 0.7918; n_D^{20} 1.3291 (99.8% methanol [6]), and the ethanol had b.p. 77.9-78.1° at 755 mm, d_4^{20} 0.8086; n_D^{20} 1.3630 (99.7% ethanol [6]). The initial ethylene-hydrogen mixture was passed at a constant speed through a vertical graduated tube filled with methanol or ethanol, before entering the catalysis tube. It was thus possible for each experiment to measure the amount of alcohol carried along with the stream of gas into the reaction space. Unreacted alcohol condensed together with reaction products in the receiver at room temperature and in that cooled at -60°, where it was found in the aqueous alcoholic layer. The amount of alcohol which had entered into the reaction was taken as the difference between the amount passed and that recovered.

For experiments with methanol the amount of unreacted alcohol was derived from the density [6] and the amount of the aqueous alcoholic layer of reaction products, which contained only insignificant admixtures of other oxygen-containing substances which could affect the accuracy of this determination. In the case of ethanol this layer contained up to 2.5 v/v-% of acids (counted as acetic acid), as was shown by direct titration with 0.1 N caustic soda solution, as well as up to 4.2% of aldehydes (counted as acetaldehyde). The aldehyde content was determined by adding hydroxylamine hydrochloride and titrating the hydrochloric acid liberated in the reaction of oxime formation. In view of the presence of these admixtures the determination of the amount of unreacted alcohol was effected as follows. The acids in the aqueous alcoholic layer were exactly neutralized by adding the appropriate amount of alkali, and the aldehyde was bound by boiling the neutral solution for 5 hrs under reflux with freshly precipitated mercuric oxide (prepared from equimolecular amounts of mercuric chloride and sodium hydroxide [7]). The solution was then distilled until all the alcohol had passed over, and the alcohol content of the distillate was derived from its density [6].

1. Hydrocondensation of methanol with ethylene

The results of the experiments with methanol and ethylene are given in Tables 1-4.

The experiments were conducted at 200°, using five specimens of catalyst (contacts 37, 38, 39, 40 and 41) in about 15 g portions in layers 40-45 cm long, in a glass tube 10 mm in diameter. Contacts 37, 38, and 39 were taken for the reaction after having previously been used in experiments on hydrocondensation of carbon monoxide with ethylene, involving mixtures of ethylene and hydrogen containing 5% of carbon monoxide (experiments 191, 193, and 196). Contacts 40 and 41 were taken freshly prepared for the reactions of hydrocondensation of methanol with ethylene.

Table 1 presents for each experiment its duration in hours, the percentage composition of the initial and final gases, the flow velocity of the initial gas in liters per liter of catalyst per hour (l/l/hr) the amount of pure methanol passed, in grams, and its flow velocity in l/l/hr (referring to the liquid alcohol).

Table 2 gives the percentage composition of the "theoretical initial gas". It is assumed that hydrocondensation of methanol with ethylene proceeds according to scheme (2), i.e., with previous decomposition of methanol according to reaction (1), to yield carbon monoxide and hydrogen. For this reason the "theoretical initial gas" consists of the initial gas ($C_2H_4 + H_2$) and of the gas ($CO + H_2$) which should be formed by the total decomposition of all the reacted methanol according to reaction (1). Table 2 also gives the percentages of methanol entering into the reaction, as well as, for a number of experiments, of ethylene, hydrogen, and carbon monoxide entering into the composition of the "theoretical initial gas" (as percentages of the initial component). The fraction of ethylene which had undergone conversion into ethane is also given in this Table.

Table 3 gives the yields of heavy oil, light oil, and Gasol (C_3 and C_4), and the total yield of condensate (not counting the aqueous layer), in ml per m³ of "theoretical initial gas". The molecular proportions of methanol, hydrogen, and ethylene entering into the hydrocondensation reaction are given for some of the experiments. It is evident that the part of the reacted methanol which entered into the hydrocondensation reaction is expressed by the fraction of reacted carbon monoxide in the "theoretical initial gas", inasmuch as the actual initial gas did not contain any carbon monoxide. The amount of carbon monoxide in the final gas represents that part of the methanol which had decomposed according to reaction (1), but had not entered into reaction (2). The fractions of reacted ethylene which had entered into the hydrocondensation reaction can be derived by subtracting from the total amount of ethylene or hydrogen which had entered into the overall reaction that part which had been used in the hydrogenation reaction with formation of ethane.

TABLE 1

Catalyst No.	Expt. No.	Duration of expt. in hrs.	Composition of the initial gas, %			Volume velocity 1/1/hr	Composition of final gas, %				Methanol introduced g	Volume velocity of methanol 1/1/hr
			C ₂ H ₄	H ₂	CO		C ₂ H ₄	H ₂	CO	C ₂ H ₆		
37	191	10	54.8	40.1	5.1	91	8.4	10.9	1.1	79.0	—	—
	192	20	57.2	42.8	0.0	68	4.0	28.5	3.1	66.4	5.28	0.01
38	193	5.5	56.1	38.9	4.8	72	1.0	40.6	0.0	58.4	—	—
	194	16	72.7	26.6	0.7	60	—	—	—	—	6.49	0.01
	195	15	68.0	32.0	0.0	54	31.1	17.9	5.5	45.5	8.01	0.02
39	196	20	63.5	31.3	5.2	70	—	—	—	—	—	—
	197	11	68.2	31.8	0.0	51	—	—	—	—	5.04	0.015
	198	11.5	70.3	29.7	0.0	58	26.7	12.6	5.6	55.1	4.91	0.01
40	199	36.0	62.3	37.7	0.0	64	15.4	14.0	5.0	65.6	15.20	0.015
41	200	16.7	60.4	39.6	0.0	67	6.5	21.3	4.7	67.5	6.41	0.01
	201	10.0	61.8	38.2	0.0	62	5.9	18.1	6.5	71.5	4.47	0.02
	202	15.0	70.7	29.3	0.0	58	—	—	—	—	6.85	0.02

TABLE 2

Expt. No.	Composition of "theoretical initial gas", %				Reacted, %			Yield of C ₂ H ₆ as % reacted C ₂ H ₄	% by wt. of methanol reacted
	C ₂ H ₄	H ₂	CO	Volume velocity 1/1/hr	C ₂ H ₄	H ₂	CO		
191	—	—	—	—	95.5	92.7	94.2	44.2	—
192	47.6	46.7	5.7	81	97.2	81.3	81.8	47.6	77.6
193	—	—	—	—	99.5	73.0	100.0	27.0	69.5
194	57.3	35.0	7.7	76	—	—	—	—	—
195	50.8	40.8	8.4	73	69.1	77.9	66.9	65.0	60.9
196	—	—	—	—	—	—	—	—	—
197	50.1	41.1	8.8	69	—	—	—	—	72.6
198	56.6	36.9	6.5	72	81.2	86.4	65.5	47.9	59.9
199	47.5	44.7	7.8	84	88.0	88.4	76.7	58.0	80.6
200	46.0	46.1	7.9	89	97.0	91.0	93.1	22.2	92.0
201	46.5	45.3	8.2	82	95.6	86.3	87.8	55.2	76.1
202	55.3	37.5	7.2	74	—	—	—	—	59.1

As is evident from Tables 1-3 hydrocondensation of methanol with ethylene proceeds at the fresh catalyst surface (contacts 40 and 41, experiments 199-202) as well as at surfaces which have previously been used in experiments with carbon monoxide (contacts 37, 38, and 39, experiments 192, 194, 195, 197, and 198). When the methanol entered the reaction tube with a volume velocity of 0.01-0.02 60-90% of it took part in the overall reaction. As is shown by the fraction of reacted carbon monoxide in the "theoretical initial gas", from 68 to 100% of the methanol entering into the reaction undergoes hydrocondensation with ethylene, and 0-32% remains in the final gas as carbon monoxide, formed by reaction (1). A "theoretical initial gas" being delivered with a volume velocity of 70-90 contained 46-57% of ethylene, 35-47% of hydrogen, and 5.7-8.8% of carbon monoxide. Of the ethylene 69-99.5% entered into reaction, and from 22 to 65% of the reacted ethylene underwent hydrogenation to give ethane. The molar ratios of methanol, hydrogen, and ethylene entering into the hydrocondensation reaction were on the average as 1:3:5, and these ratios are close to the corresponding ones for the reaction of hydrocondensation of carbon monoxide with ethylene (compare experiments 191 and 192). The total yield of condensate (not counting reaction water and unreacted alcohol) was 300-500 ml per m³ of "theoretical initial gas", or 25-30 ml/1/hr., which is also

TABLE 3

Expt. No.	Yield, ml/m ³		Gasol (g)	Yield (t + l + g)		Molecular proportions of CO (or CH ₃ OH) entering into the hydrocondensation reaction: H ₂ :C ₂ H ₄
	Heavy oil (t)	Light oil (l)		ml/m ³	ml/l/hr	
191	132.0	164.7	239.3	536.0	44.3	1:3.3:5.7
192	7.9	122.8	154.6	285.3	23.2	1:3.2:5.2
193	112.2	165.3	284.3	561.8	36.9	-
194	51.2	122.5	189.3	363.0	27.5	-
195	19.8	81.6	64.3	165.7	12.1	-
196	89.6	156.7	164.2	410.2	29.0	-
197	58.9	162.8	297.8	519.5	35.9	-
198	22.1	88.7	237.5	348.3	25.1	1:2.4:5.3
199	44.1	102.4	209.0	355.5	30.0	1:2.5:3.0
200	50.2	104.4	172.0	326.6	29.0	-
201	31.2	83.3	267.5	382.0	31.5	-
202	23.4	106.0	248.3	377.7	27.8	-

TABLE 4

Fraction	Yield % by vol.	d ₄ ²⁰	n _D ²⁰	Bromine number	% of unsaturated hydrocarbons
B.p. below 150°	67.2	0.6893	1.3925	107	67
B.p. 150-220°	15.5	0.7532	1.4245	47	48
Residue	17.3	0.8043	1.4205	19	-

close to the yields of condensate obtained by hydrocondensation of carbon monoxide with ethylene, at corresponding concentrations of carbon monoxide in the initial gas. These results show that the reaction does actually proceed according to equation (2). Some of the properties of the individual fractions of the oily products of hydrocondensation of

methanol with ethylene are given in Table 4. They are closely similar to the properties of the corresponding products of hydrocondensation of carbon monoxide with ethylene.

TABLE 5

Catalyst	Expt. No.	Duration of expt. in hr.	Composition of the initial gas, %				Comp. of final gas, in %				Ethanol introduced, g	Volume velocity of ethanol 1/1/hr
			C ₂ H ₄	H ₂	CO	Volume velocity 1/1/hr	C ₂ H ₄	H ₂	CO	C _n H _{2n+2} + s		
44	213	15	44.2	55.8	0.0	103	2.0	37.9	2.2	57.9	26.4	0.11
	214	15	46.1	53.9	0.0	108	1.1	36.8	1.1	61.0	19.4	0.06
	215	15	57.2	42.8	0.0	112	12.5	19.7	3.1	64.7	16.8	0.07
45	216	10	58.7	41.3	0.0	62	4.5	17.1	2.0*	73.7	12.0	0.04
	217	5	50.9	49.1	0.0	59	4.5	14.9	1.5**	77.6	6.8	0.05

* The final gas of experiment 216 also contained 2.7% CO₂.

** The final gas of experiment 217 also contained 1.5% CO₂.

2. Hydrocondensation of ethanol with ethylene

The results of experiments on the hydrocondensation of ethanol with ethylene are given in Tables 5-7.

The experiments were conducted as for methanol, at 200°. Two specimens of catalyst were taken (contacts 44 and 45); the experiments were done with previously unused catalysts. The data of Tables 5, 6, and 7 correspond to those of Tables 1, 2 and 3 for methanol.

TABLE 6

No. of experiment	Composition of "theoretical initial gas", %					Reacted, in %			Yield of C_2H_6 as % of reacted C_2H_4	% by weight of ethanol reacted
	C_2H_4	H_2	CO	CH_4	Volume velocity 1/1/hr.	C_2H_4	H_2	CO		
213	24.8	46.0	14.6	14.6	183	97.3	72.5	93.7	18.2	72.6
214	29.9	46.7	11.7	11.7	166	98.6	73.0	96.9	31.5	70.9
215	42.4	40.4	8.6	8.6	151	90.5	84.1	88.3	32.4	58.3
216	39.2	38.6	11.1	11.1	93	96.4	85.3	94.8	32.3	71.6
217	32.6	43.4	12.0	12.0	94	94.8	86.8	95.2	57.0	69.0

TABLE 7

No. of experiment	Yield, ml/m ³			Yield (t + l + g)	
	Heavy oil (g)	Light oil (l)	Gasol (g)	ml/m ³	ml/1/hr.
213	11.7	87.4	128.1	227.2	35.4
214	6.2	68.2	161.2	235.6	34.5
215	0.0	37.4	209.0	246.4	34.0
216	28.7	121.4	115.0	265.1	22.0
217	26.0	104.0	78.0	208.0	17.0

TABLE 8

Fraction	Yield % by vol	d_4^{20}	n_D^{20}	Bromine number	% of unsaturated hydrocarbons
b.p. below 150°	80	0.7124	1.3830	55	38
b.p. 150-210°	11.6	0.7129	1.4239	36	30
Residue, b.p. above 210°	4.2	-	-	-	-

We assume that the hydrocondensation of ethanol with ethylene proceeds according to scheme (4), i.e., with preliminary decomposition of ethanol according to reaction (3), giving carbon monoxide, hydrogen, and methane. For this reason the "theoretical initial gas" consists of the initial gas ($C_2H_4 + H_2$) and of the gas which should be formed as a result of reaction (3) from that amount of ethanol represented by the difference between alcohol introduced and alcohol recovered unchanged or as acetaldehyde and acetic acid. The yields of condensate given in Table 7 are calculated on "theoretical initial gas" taken, the volume of methane formed being subtracted.

The data of Tables 5-7 show that hydrocondensation of ethanol with ethylene takes place. 58.3-72.6% of the ethanol entering the reaction zone with a flow velocity of 0.04-0.11 entered into reaction. As is shown by the ratio of reacted carbon monoxide in the "theoretical initial gas", 88-97% of the ethanol which enters into reaction takes part in the hydrocondensation reaction, and only 3-12% of it remains in the final gas as carbon monoxide, which may have been formed by reaction (3). As appears from Table 6, the "theoretical initial gas" had the composition: ethylene 25-42, hydrogen 39-47, carbon monoxide 9-15, and methane 9-15%. 90-99% of the ethylene entered into reaction, and 18-57% of this amount was hydrogenated to ethane. The total yield of condensate (not counting the aqueous alcoholic layer) was 208-246 ml per m³ of "theoretical initial gas" (subtracting methane), or 17-35 ml/1/hr.

Some of the properties of the individual oily fractions of the product of hydrocondensation of ethanol with ethylene are given in Table 8. The somewhat high values found for the density, and the low values for the refractive index of the fraction of b.p. below 150° are due to presence of oxygen-containing products, as is confirmed by boiling the fraction with sodium for 3 hours, after which the density becomes 0.7066, and the refractive index 1.3862.

SUMMARY

1. Similarly to carbon monoxide, methanol and ethanol promote the reaction of condensation of ethylene and hydrogen, and at the same time enter into the hydrocondensation reaction with ethylene.
2. The total yield of condensate (not counting water and unreacted alcohol) amounts to 17-35 ml per liter of catalyst per hour.
3. The experimental results confirm the view that the process involves the preliminary decomposition

of the alcohols, with production of carbon monoxide and hydrogen, which then, through the intermediate stage of formation of methylene radicals, enter as usual into the reaction of hydrocondensation with ethylene.

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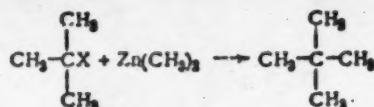
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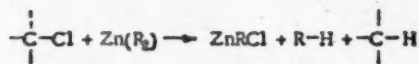
SYNTHESIS AND PROPERTIES OF TETRAPROPYLMETHANE, TETRABUTYLMETHANE, AND TETRAHEXYLSILANE

A. D. Petrov and E. A. Chernyshev

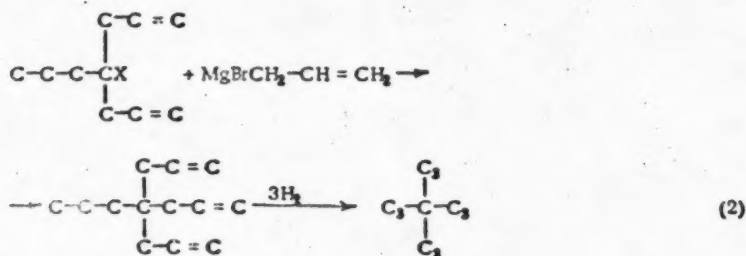
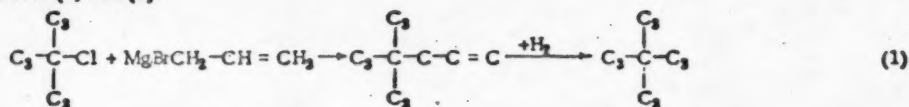
The tetraalkylmethane series has been insufficiently studied. Its first member, tetramethylmethane, was obtained by Lvov [1] in 1870, by the reaction: *



This hydrocarbon was next prepared by a Grignard synthesis [2], but Morgan [3] was unable to prepare the second member, tetraethylmethane, by this method, and had to use Lvov's method for the purpose. Karrer and Ferri [4] attempted to prepare tetra-*n*-butylmethane by this same method, notwithstanding that Vagner [5] and Pavlov [6] had pointed out the tendency of the higher zinc alkyls to decompose with formation of olefinic hydrocarbons and with reduction of the tertiary chloride by the reaction:

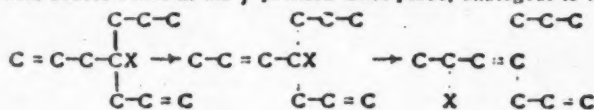


As we showed in our preceding paper [7], Karrer and Ferri actually obtained tributylmethane, which they mistakenly identified as tetrabutylmethane. In the same paper we described the synthesis of tetrapropylmethane by reactions (1) and (2):



The yield obtained by reaction (1) was 10%, and by reaction (2) 30%.

The mixture of products obtained by reactions (1) and (2) was subjected to hydrogenation. The hydrogenation product was distinguished by its very low freezing point, which led us to suspect that tetrapropylmethane is obtained only by reaction (1), and that in reaction (2) a hitherto unknown reaction of isomerization of the alkyl halide with double bonds in the γ -position takes place, analogous to the allyl rearrangement:



In this research we repeated reaction (2), and by oxidation of the product of synthesis (α -methylvaleric

acid and methyl propyl ketone were isolated and identified) we showed that this assumption was correct, and that hydrogenation of the product of reaction (2) gives 4-methyl-6-propylnonane, not tetrapropylmethane.

In view of the low yield of tetrapropylmethane by reaction (1) we investigated the reaction of condensation with C_3MgX , with a saturated alkyl halide (a) at elevated temperatures and (b) in presence of the condensing agent $HgCl_2$. We applied these findings to the synthesis of tetrabutylmethane, which has not previously been described. We were not, however, able to obtain tetrahexylmethane, partly because of the instability of the halohydrin of trihexylcarbinol, and partly because with increase in the length of the radical R of $MgRX$ a form of decomposition analogous to that found for zinc propyl or butyl takes place. As a result we obtained only trihexylmethyl chloride and the olefin produced by elimination of HCl from it.

We then, bearing in mind Whitmore's remark, that "the synthesis of readily available silanes with quaternary silicon atoms may serve in place of their much more difficultly preparable carbon analogs for the elucidation of the properties of such structures", turned to the synthesis of tetrahexyl- and tetraoctylsilane. We here bore in mind the closeness of the boiling points and the densities, but not the freezing points, since Bygden [9] has shown that hexamethyldisilane freezes at 12° , while the f.p. of its carbon analog is at 100° . The physical constants of the hydrocarbons prepared by us, and of their structural analog tetrahexylsilane, are given in Table 1.

TABLE 1
Physical constants of some tetraalkylmethanes and silanes

Compound	Freezing point	Boiling point	Pressure mm	n_D^{20}	d_4^{20}
Tetrapropylmethane	-26	60-62	6	1.4322	0.7706
Tetrabutylmethane	-6	103-104	6	1.4440	0.7835
Tetrahexylsilane	-30	178-179	5	1.4532	0.8144

We were able by the action of $C_6H_{13}MgBr$ on $SiCl_4$ to obtain only $(C_6H_{13})_2SiCl_2$. Tetrahexylsilane was prepared by heating $SiCl_4$ with LiC_6H_{13} at 90° . Tetraoctylsilane could not be obtained by the latter method, the product being $(C_8H_{17})_2SiCl_2$. Thus LiC_6H_{13} differs from LiC_8H_{17} when heated at 90° with $SiCl_4$ in that only three of the chlorine atoms are replaced, evidently owing to

the considerable steric hindrance developed by the larger radical.

EXPERIMENTAL

1. Tetrapropylmethane was obtained by the condensation of the chlorohydrin of tripropylcarbinol with propyl bromide in presence of Mg . The chlorohydrin was prepared by saturating the carbinol with dry HCl at 0° ; yield 63%. 2,2-Dipropylbutyl chloride has not previously been described; it boiled at $54-56^\circ/7$ mm, n_D^{20} 1.4378; d_4^{20} 0.8676; found MR_D 53.38; calculated MR_D 53.24.

Found %: Cl 19.58; 19.67
 $C_{16}H_{34}Cl$. Calculated %: Cl 19.85

The condensation reaction was conducted as follows. The Grignard reagent was prepared in the usual way from 95 g of propyl bromide, 18.5 g of magnesium, and 200 ml of absolute ether. 3.5 g of mercuric chloride was added, followed by 68 g of tripropylmethyl chloride, added drop by drop during 8 hours at $20-25^\circ$, and the reaction mixture was left over night, after which it was boiled for 2 hours, and treated with 10% HCl . The ethereal layer was dried with Na_2SO_4 , and the ether was distilled off on a water-bath. The residue was fractionally distilled in vacuo, giving two fractions: Fraction I, 34.5 g, b.p. $33-35^\circ/6$ mm, n_D^{20} 1.4374, d_4^{20} 0.7682, was 4-propylhept-3-ene, produced by elimination of HCl from the chloride; published constants [10] are b.p. $160-162^\circ/734$ mm, n_D^{20} 1.4386.

Fraction II (12.0 g), b.p. $60-62^\circ/6$ mm, was tetrapropylmethane. It was treated with concentrated H_2SO_4 , water, sodium carbonate solution, dried, boiled with Na , and redistilled, giving 9.2 g, b.p. $60-61^\circ/6$ mm, n_D^{20} 1.4322, d_4^{20} 0.7706, m.p. -26.5° , calculated MR_D 62.23, found MR_D 62.07, yield 12.7%.

Found %: C 84.30; 84.30; H 15.30; 15.10
 $(C_3H_7)_4C$. Calculated %: C 84.66 H 15.34

The same method was applied in a different variant, as follows. The ether was distilled off from the Grignard compound, an equivalent amount of isopentane was added, followed by tripropylmethyl chloride at $80-90^\circ$; the yield of tetrapropylmethane was 11.5%. Altogether, 15 g of tetrapropylmethane was prepared.

2. Tetrabutylmethane. Tributylmethyl chloride was prepared by saturating the carbinol with HCl at 0° (70% yield). It has not previously been prepared; its constants are: b.p. 102-103°/7 mm, n_D^{20} 1.4465, d_4^{20} 0.8744, found MR_D 66.70, calculated MR_D 67.09.

Found %: Cl 16.23; 16.08
 $C_{12}H_{27}Cl$ Calculated %: Cl 16.22

According to the first variant of the synthesis of tetrabutylmethane the reaction was conducted under the same conditions as for tetrapropylmethane, giving a 22.4% yield. When the reaction was conducted at higher temperatures (80-90°), without the addition of mercuric chloride, the yield was 13.5%. According to a third variant the ether was distilled off from the Grignard compound, isooctane and 2-3 g of mercuric chloride were added, the mixture was warmed to 80-90°, and tributylmethyl chloride was gradually added, giving a 17% yield of tetrabutylmethane. Altogether 18 g of tetrabutylmethane was obtained, b.p. 103-104°/6 mm, m.p. -6°, n_D^{20} 1.4440, d_4^{20} 0.7935, found MR_D 80.48, calculated MR_D 80.68.

Found %: C 84.88; 85.03; H 15.02; 15.01
 $(C_4H_9)_4C$. Calculated %: C 85.00 H 15.00

3. Attempted synthesis of tetrahexylmethane. Tri-n-hexylcarbinol and tri-n-hexylmethyl chloride were synthesized as follows: they have not previously been prepared. A mixture of 350 g of n-hexyl bromide, 170 g of ethyl oenanthat, and 350 ml of absolute ether was added drop by drop to 48 g of magnesium in 350 ml of absolute ether, at 20-30°, the mixture was left overnight, boiled for 2 hours, and poured on ice. 10% HCl was then added, and the ethereal layer was dried with Na_2SO_4 . The ether was distilled off, and the residue was twice distilled, collecting the fraction of b.p. 153-154°/4.5 mm; yield 80.5 g (33%), b.p. 153-154°/4.5 mm, n_D^{20} 1.4496; d_4^{20} 0.8365; found MR_D 91.17; calculated MR_D 91.46.

Found %: C 80.11; 80.26; H 14.03; 14.29
 $(C_6H_{13})_3COH$. Calculated %: C 80.28; H 14.08

Trihexylcarbinol was saturated with dry HCl at 0°, and the product was washed a few times with ice-water, and residual dissolved HCl was removed by bubbling nitrogen through it. The chloride could not be distilled, as it decomposed, with copious evolution of HCl, when heated at 70-80°/3 mm. The undistilled trihexylmethyl chloride, yield 83%, had the following properties: n_D^{20} 1.4530, d_4^{20} 0.8661, found MR_D 84.40, calculated MR_D 84.80.

Found %: Cl 10.94; 10.74
 $C_{19}H_{39}Cl$. Calculated %: Cl 11.73

All further operations were performed with undistilled chloride.

Three attempts were made to synthesize tetrahexylmethane, by adding trihexylmethyl chloride to magnesium hexyl chloride in presence of small amounts of mercuric chloride at 40°, 20°, and 0°. The reaction was also attempted at 10°, in presence of 1 mole of mercuric chloride per mole of hexyl bromide, and at 65°, in absence of mercuric chloride. In all cases the sole product was 7-hexyltridec-6-ene, being the product of elimination of hydrogen chloride from trihexylmethyl chloride; not even a trace of tetrahexylmethane was formed. Attempted condensation of trihexylmethyl chloride with butyl bromide gave the same result.

7-Hexyltridec-6-ene has not previously been described. It has the following properties: b.p. 149-150°/5.5 mm, freezing point -80°, n_D^{20} 1.4490, d_4^{20} 0.7957, found MR_D 89.66, calculated MR_D 89.47.

Found %: C 85.62; 85.57; H 14.40; 14.35
 $C_{19}H_{38}$. Calculated %: C 85.71; H 14.29

4. Tetrahexylsilane was prepared by the action of silicon tetrachloride on excess of hexyl-lithium. The lithium-organic compound was prepared from 216 g (1.3 moles) of hexyl bromide and 18.3 g (2.62 moles) of lithium, in ether, and 18.5 g (0.109 moles) of silicon tetrachloride was added, cooling the mixture in ice. It was then stirred for 2 hours at room temperature, the ether was distilled off, and the residue was heated at 90-100°, with stirring, for a further 5 hours, after which it was left over night. It was then treated with acid, in the usual way, and shaken with ether, the ethereal layer was washed and dried, the ether was distilled off, and the residue was washed with concentrated H_2SO_4 , sodium carbonate solution and water, dried, and vacuum distilled, giving two fractions:

Fr. I, b.p. 178-179°/5.0 mm., 12 g
Fr. II, b.p. 223-225°/4.5 mm., 16.5 g

Fraction I consisted of tetrahexylsilane, b.p. 178-179°/5 mm, m.p. -30°, n_D^{20} 1.4532, d_4^{20} 0.8144, found SiR_D 7.01, yield 30%.

Found %: C 78.71; 78.74; H 13.93; 13.93; Si 7.26; 7.14
 $(\text{C}_6\text{H}_{13})_4\text{Si}$. Calculated %: C 78.25 H 14.13; Si 7.60

Fraction II was hexahexyldisiloxane, b.p. 223-225°/4.5 mm, n_D^{20} 1.4547, d_4^{20} 0.8398, found SiR_D 6.9, yield 26%.

Found %: C 74.12; 74.59; H 13.45; 13.60; Si 9.75; 9.32
 $\text{C}_{12}\text{H}_{26}\text{Si}_2\text{O}$. Calculated %: C 74.23; H 13.40; Si 9.62

An attempted synthesis of tetrahexylsilane from magnesium hexyl bromide and tetraethoxysilane did not give the expected product, even when the reaction mixture was boiled in paraffin solution at 170-180° for 15 hours. After the usual treatment of the reaction mixture the following two fractions were obtained:

Fr. I, b.p. 150-152°/4.5 mm

Fr. II, b.p. 223-226°/4.5 mm

Fraction I was found to consist of ethoxytriethylsilane, yield 40%, b.p. 150-152°/4.5 mm, n_D^{20} 1.4462, d_4^{20} 0.8298, found SiR_D 7.1.

Found %: C 72.73; 73.09; H 13.61; 13.48; Si 8.14; 8.16
 $\text{C}_{12}\text{H}_{24}\text{SiO}$. Calculated %: C 73.17; H 13.41; Si 8.53

Fraction II was hexahexyldisiloxane, yield 10.7%. The product obtained when tetraethoxysilane was taken instead of silicon tetrachloride was hexahexyldisiloxane, in 56% yield. Tetrahexylsilane was not obtained.

5. Attempted synthesis of tetraoctylsilane. The reaction was conducted under the same conditions, and taking the same molecular proportions of reagents as in the preparation of tetrahexylsilane through the lithium-organic compound. Although tetrahexylsilane was thus obtained in 30% yield, tetraoctylsilane was not produced at all. The final product of the reaction was found to be hexaoctyldisiloxane, in 47% yield, b.p. 320-322°/8 mm, n_D^{20} 1.4575, d_4^{20} 0.8427, found SiR_D 6.9.

Found %: C 76.37; 76.24; H 13.49; 13.51; Si 7.26; 7.30
 $\text{C}_{16}\text{H}_{34}\text{Si}_2\text{O}$. Calculated %: C 76.50 H 13.60; Si 7.47

SUMMARY

1. Tetrapropylmethane and tetrabutylmethane, which have not previously been prepared, were obtained by a modified Grignard-Würtz synthesis.
2. We were not able, because of the instability of trihexylmethyl chloride, to achieve the synthesis of tetrahexylmethane under the given conditions.
3. Tetrahexylsilane, which has not previously been described, was prepared from SiCl_4 and $\text{LiC}_6\text{H}_{13}$. The analogous reaction with $\text{LiC}_8\text{H}_{17}$ did not proceed beyond formation of $(\text{C}_8\text{H}_{17})_2\text{SiCl}_2$.

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BEHAVIOR OF γ -HALOGENODIALKENYLS IN THE GRIGNARD-WÜRTZ SYNTHESIS

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The literature gives only very scanty indications relating to the application in magnesium-organic syntheses of halogenodialkenyls with a double bond in the α -position relative to the halogen. One of the earliest papers dealing with this problem is that of Krestinsky [1], who showed that the action of magnesium on isocrotyl bromide gave only a very small yield of Grignard reagent, large amounts of isobutylene being evolved. With acetaldehyde, magnesium isocrotyl bromide gives the appropriate secondary alcohol in 14% yield only, and with isobutyraldehyde in 15.8% yield. He also prepared the Grignard reagent from the secondary halogenoalkenyl 3-bromo-2-methylbut-2-ene, and showed that it reacted with acetaldehyde to give the desired alcohol, although he does not state in what yield. The Grignard reagent could not be obtained at all from vinyl bromide and magnesium, from which a quantitative yield of ethylene and acetylene was given. Kogerman [2] was also unable to prepare magnesium vinyl bromide. In studying the Grignard synthesis of penta-1,4-diene from allyl bromide and vinyl bromide he found that the desired diene was obtained in small yield (15%), only when magnesium-copper alloy was used. Kirman [3] obtained the magnesium-organic compound from 1-bromohept-1-ene, in 25% yield, and by treating it with water he obtained hept-1-ene, in a yield of 20% calculated on the amount of bromide taken.

Karash and Fuchs have recently obtained a series of hydrocarbons in good yield by the reaction of vinyl bromides with magnesium phenyl and benzyl bromide in presence of the salts CoCl_2 , CuCl_2 , and GrCl_3 [4]. Without these salts, however, the reaction either did not proceed at all, or only very small yields (less than 5%) were obtained. These data provide support for the view that the presence of a double bond in the α -position to the halogen causes considerable lowering of the reactivity of alkyl halides in the Grignard synthesis.

On the other hand, the presence of a double bond in the β -position to the halogen considerably augments the reactivity of alkenyl halides; thus Levin [5] obtained a number of branched-chain olefins in yields of over 30% from 1,1,3-trimethylbutadiene hydriobromide and RMgX , whereas saturated alkyl halides of the same structure do not enter into the Grignard-Wurtz reaction at all. Young and Roberts [6] showed that primary and secondary alkenyl β -halides give even higher yields, of the order of 80-85%, in the Grignard and Grignard-Wurtz reactions. However, the use of alkenyl β -halides for the Grignard synthesis of individual hydrocarbons and alcohols is complicated by the circumstance that they tend to isomerize, with shift in the position of both the double bond and the halogen, either during distillation of the alkenyl halide, or in many cases during the actual reaction.

Only a few papers have been published on the use of alkenyl γ -halides. Schinz and Simon [7] obtained the desired alcohol in 26% yield from 5-bromo-2-methylpent-2-ene and α -methylacrolein, and they showed that the saturated bromide of the same structure gave higher yields than this. Goethals [8] obtained the magnesium-organic compound of 5-chloropent-2-ene which with acrolein gave octa-1,6-dien-3-ol, in 50% yield. The comparatively high yields of alcohols obtained in the last two cases may be due to the circumstance that primary γ -halides were taken, but chiefly because the synthesis was performed with active carbonyl compounds with a double bond in the β -position to the carbonyl group.

The behavior of primary, secondary, and tertiary alkenyl γ -halides in the Grignard-Wurtz reaction has not yet been studied; it is the subject of the present communication.

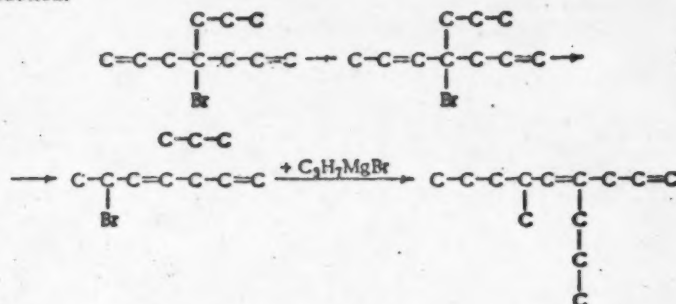
We took 4-bromobut-1-ene, 4-bromopent-1-ene, and 4-bromo-4-methylpent-1-ene, and we found that these primary, secondary, and tertiary alcohols do not enter into the Grignard-Wurtz reaction. 4-Bromopent-1-ene is recovered unchanged when taken for reaction with CH_3MgBr , with only a little splitting off of HBr . 4-Bromopent-1-ene similarly does not react with $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$, whereas with the corresponding saturated secondary halide (taken as a Grignard reagent) and allyl bromide the product was 4-methylhept-1-ene; 4-bromo-4-methylpent-1-ene also did not react with CH_3MgBr . The same result was obtained with 4-chloro-4-methylpent-1-ene instead of the bromide, and $\text{Zn}(\text{CH}_3)_2$ instead of CH_3MgBr . The magnesium-organic compound given by 4-bromo-4-methylpent-1-ene similarly did not react with methyl bromide, or

even with so reactive an alkenyl halide as is allyl chloride. Yet CH_3MgBr reacted with the saturated bromide of the same structure (4-bromo-4-methylpentane), giving 2,2-dimethylpentane in 15% yield.

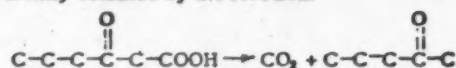
Magnesium γ -butenyl bromide did not react with tributylmethyl chloride, while magnesium butyl bromide gave tetrabutylmethane in 15% yield under the same conditions.

We have shown in an earlier paper that a condensation product is obtained from 4-bromo-4-methylhepta-1,6-diene and magnesium propyl bromide [9], and hydrogenation of the diene so obtained should be expected to yield tetrapropylmethane. However, the low reactivity of alkenyl γ -halides in Grignard-Würtz reactions, and the very low freezing point ($< -70^\circ$) of the product of hydrogenation of the diene (the freezing point of tetrapropylmethane obtained by a different method is -26°), obliged us to suppose that a hitherto unknown γ -rearrangement of the unsaturated alkyl γ -halide has here taken place.

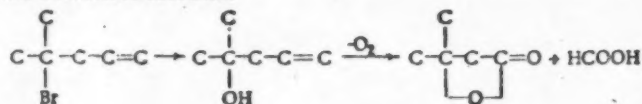
The present paper describes a repetition of this reaction, with oxidation of the condensation products; formic and methylvaleric acid and methyl propyl ketone were identified among the oxidation products, showing that the following rearrangement must have taken place either during preparation of the bromide or during the condensation reaction:



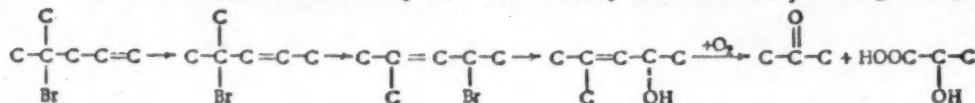
Methyl propyl ketone was evidently obtained by the reaction:



A study of the oxidation of 4-bromo-4-methylpent-1-ene showed that this tertiary halide only to a small extent undergoes isomerization to β -halide, the formation of which is a result of isomerization of the allyl to the propenyl radical. Among the products of oxidation with 1% aqueous KMnO_4 were found β -methyl- β -butyrolactone, formic acid, acetone, and lactic acid, of which the first two products were obtained by hydrolysis and oxidation of the non-isomerized substance



Acetone and lactic acid could only have been formed by oxidation of the γ -rearrangement product:



Acetone could have been obtained by oxidation of the product of elimination of HBr from the bromide, but this could not have taken place under the conditions of the oxidation reaction; it takes place only after several hours of boiling of the bromide with strongly alkaline solutions [10].

The small degree of isomerization of the allyl into the propenyl radical was evidently not augmented by the action of the Grignard reagents on this bromide, and this was the reason why this halide was not, in contrast to 4-bromo-4-propylhepta-1,6-diene, able to enter into the Grignard-Würtz reaction.

A stronger tendency towards isomerization of allyl to propenyl radicals in presence of Grignard reagents is observed as the number of allyl groups in the bromide molecule increases, as in the cases of 4-bromo-4-methyl-

pent-1-ene and 4-bromo-4-propylhepta-1,6-diene. This corresponds with the enhancement of this type of isomerization observed in the dehydration of allylic alcohols and glycols. We know [11] that the isomerization of allyl to propenyl radicals has never been observed in the dehydration of dimethylallylcarbinol, whereas dehydration of 1,1,6,6-tetraallylhexanediol [12] gives 1,1,6,6-tetrapropenylhexa-1,5-diene.

EXPERIMENTAL

1. Reaction of the Grignard reagent from dimethylallylmethyl bromide with methyl bromide. 120 g of the bromide was added gradually to 16 g of activated magnesium at 10°, and methyl bromide was passed into the product. After the usual treatment, and after elimination of the ether, a small yield of product (3.5 g) was obtained, boiling at 70-80°. After hydrogenation it had b.p. 73-80°, n_D^{20} 1.3761, d_4^{20} 0.6684. Owing to its small amount, and to the presence therein of fluorescent admixtures, the product could not be subjected to spectrum analysis, but it seems probable from its physical constants, given above, that it is isohexane. The ethereal distillate contained isohexene, identified as the dibromide, b.p. 98-99°, n_D^{20} 1.5110; d_4^{20} 1.5500.

	Found %:	Br 66.09
$C_6H_{12}Br_2$	Calculated %:	Br 65.53

A variant of this experiment consisted in adding 70 g of dimethylallylmethyl chloride to a Grignard compound prepared from 24 g of magnesium and methyl chloride. The mixture, after the usual treatment, gave 3 g of a product which after hydrogenation had b.p. 70-80°, d_4^{20} 0.6672, n_D^{20} 1.3765, i.e., it was the same as obtained in the preceding experiment; 28 g (40%) of chloride was recovered unchanged from the reaction mixture. The process was repeated in presence of $HgCl_2$ as activator. An ethereal solution of CH_3MgBr was added to 74 g of dimethylallylmethylchloride and 10 g of $HgCl_2$, and after the usual treatment 13.5 g of the initial chloride was recovered unchanged, and a crystalline precipitate was obtained, which rapidly darkened on exposure to the air, and appeared to be a mercury-organic compound. 4,4-Dimethylpent-1-ene was not obtained.

2. Reaction of CH_3MgBr with 2-chloro-2-methylpentane. 2-Chloro-2-methylpentane, prepared from the corresponding alcohol and HCl , had b.p. 110-112°, n_D^{20} 1.4195. 131 g of 2-chloro-2-methylpentane was added to an ethereal solution of CH_3MgBr prepared from 48 g of magnesium, and after the usual treatment, and elimination of unsaturated products, 16 g of a product (15% yield) was obtained. It had b.p. 78-79°, n_D^{20} 1.3820, d_4^{20} 0.6730, bromine no. 0, found MR_D 34.51, calculated for C_7H_{14} , MR_D 34.53; spectrum analysis showed the presence of 2,2-dimethylpentane only in this fraction.

This experiment was repeated, taking 105 g of 2-chloro-2-methylpentane and 8 g of $HgCl_2$. The same product was obtained (12% yield) as in the previous reaction, b.p. 79-80°, n_D^{20} 1.3820, d_4^{20} 0.6727, bromine no. 0.

3. Reaction of CH_3MgBr with 4-bromopent-1-ene. Methylallylcarbinol was prepared as described by Stohr [13]; it boiled at 115-117°. (Stohr gives 115-116°). The corresponding bromide, prepared under the same conditions as for dimethylallylmethyl bromide, boiled at 111-112°, n_D^{20} 1.4520, d_4^{20} 1.2417, experimental MR_D 32.8, calculated for C_5H_8Br MR_D 32.6. The magnesium-organic compound was obtained from methyl bromide and 24 g of activated magnesium, and 55 g of 4-bromopent-1-ene was added gradually to it. The mixture was then left overnight, and was heated at the b.p. of ether for 2 hrs. After the usual treatment 45 g of bromide was recovered unchanged; no fraction corresponding to 4-methylpent-1-ene was obtained.

4. Reaction of $CH_2=CH-CH_2MgBr$ with 4-bromopent-1-ene. 50 g of 4-bromopent-1-ene was added to $CH_2=CH-CH_2MgBr$, prepared from 60 g of $CH_2=CH-CH_2Br$ and 11 g of magnesium (a threefold excess), and the mixture was kept at 30° for 80 hrs. After the usual treatment, and after distilling off the ether, the residue was distilled, giving a product, b.p. 110-125°, n_D^{20} 1.4510, d_4^{20} 1.0653. This fraction appears to consist chiefly of the original bromide, but since the hydrocarbon which might arise in this reaction, 4-methylhepta-1,6-diene, boils within the same range, 110.5-110.9°, the product was treated with alcoholic alkali, in order to remove the original bromide. The whole of the residue reacted with the alkali, 4-methylhepta-1,6-diene not being found.

5. Reaction of $CH_3CH_2CH_2CH(CH_3)MgBr$ with allyl bromide. 50 g of allyl bromide was added to the magnesium-organic compound prepared from 60 g of 2-bromopentane and 16 g of magnesium, and the mixture was heated for 80 hrs at 30°. After the usual treatment, 3.7 g of a product was obtained, b.p. 110-113°, n_D^{20} 1.4150, d_4^{20} 0.7296, and 30 g of allyl bromide was recovered (b.p. 69-71°). Since the density of the product obtained by us was higher than that of 4-methylhept-1-ene (the following constants are recorded for this: b.p. 112.6-113°, d_4^{20} 0.7183, n_D^{20} 1.4099 [14]), and since it gave a qualitative reaction for halogen, it was boiled with sodium, after which its physical constants approximated closely to those of 4-methylhept-1-ene (b.p. 112-113°, d_4^{20} 0.7191, n_D^{20} 1.4105, experimental MR_D 39.08, MR_D calculated for C_8H_{16} 38.68, iodine no. 221.2, calculated iodine no. for C_8H_{16} 226.4).

6. Oxidation of 4-bromo-4-methylpent-1-ene. 4-Bromo-4-methylpent-1-ene was prepared from PBr_3 and dimethylallylcarbinol in pyridine at 0° , followed by heating for 3-4 hr. After washing with water and redistilling it boiled at $42-47^\circ$ at 30 mm, $120-125^\circ$ at 760 mm, n_D^{20} 1.4650, d_4^{20} 1.2001, experimental MR_D 37.97, MR_D calculated for $\text{C}_6\text{H}_{11}\text{Br}$ 37.21.

40 g of the bromide was oxidized with 1% KMnO_4 solution at 0° [15], 80 g of KMnO_4 being used. The solution was steam-distilled, to remove neutral products. The aqueous distillate was evaporated down to a volume of 50 ml, and this was saturated with potash. The oily layer was separated and distilled, giving the fractions:

Fraction I, b.p. $58-60^\circ$

Fraction II, b.p. $60-70^\circ$

Residue, density > 1 .

Fractions I and II, and the residue, were treated with 2,4-dinitrophenylhydrazine. The fractions gave crystalline precipitates, but the residue did not react. The 2,4-dinitrophenylhydrazone given by Fraction I melted at $123-124^\circ$, mixed m.p. with the 2,4-dinitrophenylhydrazone of acetone $123.5-124.5^\circ$. The 2,4-dinitrophenylhydrazone of Fraction II melts at 120° .

The residue from steam-distillation of the oxidation products was filtered from MnO_2 , acidified, and again steam-distilled. The volatile acids included formic acid (1.176 g), b.p. $103-105^\circ$, n_D^{20} 1.3720, NaOH equivalent wt. 88.7, calculated for HCOOH 89.0.

A small amount of lactic acid was also found, identified by the iodoform reaction, and by analysis of its silver salt:

Found %: Ag 55.22

$\text{C}_3\text{H}_5\text{O}_2\text{Ag}$. Calculated %: Ag 54.82

Oxidation of dimethylallylcarbinol with 4% KMnO_4 did not lead to production of acetone. β,β -Dimethylacrylic acid (oxidation of which gives acetone) is obtained from $(\text{CH}_3)_2\text{CBrCH}_2\text{COOH}$ only by boiling with phenol or KOH [10].

Non-volatile acids. The residue after elimination of volatile acids was evaporated down, treated with 25-30 % sulfuric acid, and extracted with a large volume of ether. The residue after evaporation of the ether was fractionally distilled in vacuum, giving the following fractions:

Fraction I, b.p. $70-75^\circ$ at 10 mm

Fraction II, b.p. $75-78^\circ$ at 10 mm, d_4^{20} 0.9973; n_D^{20} 1.4430

C 58.54%; H 8.10%; equivalent 109

In addition, a crystalline product, m.p. $68-69^\circ$, C 59.9%, H 7.95%, was obtained; its m.p. was not depressed when mixed with dimethylacrylic acid.

Fraction I gave a silver salt, Ag 48.96%, calculated for $\text{C}_5\text{H}_7\text{O}_2\text{Ag}$ Ag 48.0%.

Fraction II is a mixture of hydroxyvaleric acid with valerolactone. Valerolactone and dimethylacrylic acid are always formed from the corresponding hydroxyvaleric acid when distilled in vacuum.

7. Examination of the product of reaction of 4-bromo-4-propylhepta-1,6-diene with propyl magnesium bromide. Diallylpropylcarbinol was saturated with dry HBr at $80-90^\circ$, to give 4-bromo-4-propylhepta-1,6-diene, 45 g of which was taken with 10 g of magnesium and 50 g of propyl bromide, in boiling ethereal solution, as described in our previous paper [9]. The product (6.2 g, 17% yield) is tridecadiene, b.p. $98-104^\circ$ at 20 mm, n_D^{20} 1.4464, $\text{C}_{13}\text{H}_{24}$.

6 g of tridecadiene was oxidized with 1% KMnO_4 solution, the MnO_2 was filtered off, and the filtrate was made strongly acid and boiled for several hours in order to effect decarboxylation of any β -keto-acids which might have been formed. The solution was then alkalized and steam-distilled, and the distillate was extracted with ether, to remove neutral products. The ether was distilled off, and the residue was fractionated; practically all of it came over at $98-104^\circ$ (most of it at $99-101^\circ$), yield 1.7 g. This was shown to be methylpropyl ketone, identified as the 2,4-dinitrophenylhydrazone, m.p. 142° , (published m.p. 144° [16]), not depressing the m.p. of a known specimen.

The residue from steam-distillation was evaporated down and acidified with dilute sulfuric acid. The layer of acidic products forming was separated, and the aqueous layer was extracted with ether. The acidic layer was dissolved in the ethereal extract, which was dried, the ether was distilled off, and the residue was fractionated, giving 0.4 g of a fraction of b.p. 99-103°, and 2.3 g of a fraction boiling at 191-196° (most of it at 193-194°), n_D^{20} 1.4117. The first fraction gave a precipitate of calomel when treated with mercuric chloride, showing that it was formic acid. The second fraction was α -methyl-valeric acid (recorded constants, b.p. 192-193.6°, n_D^{20} 1.4136 [17]), the silver salt of which was analyzed:

Found %: Ag 47.88
 $C_6H_{11}O_2Ag$. Calculated %: Ag 48.4

The amide of this acid melted at 77°, published m.p. 78° [17]. No other acids were found. It follows that 4-bromo-4-propylhepta-1,6-diene does not enter into the reaction, as could have been expected; its rearrangement product 6-bromo-4-propylhepta-1,4-diene reacts instead. The rearrangement may have taken place during the synthesis of the bromide, at the temperatures involved, or it may have occurred during the Grignard-Wurtz reaction.

5. Reaction between γ -butenyl magnesium bromide and 5-chloro-5-butylnonane. PBr_3 in pyridine and but-3-en-1-ol were allowed to react under the conditions described by Juvala [18], to give butenyl γ -bromide, b.p. 97-99°, d_4^{20} 1.3247; n_D^{20} 1.4638; published constants [18]: b.p. 98.5-99° at 758 mm; d_4^{20} 1.3230; n_D^{20} 1.46215 [18].

The magnesium-organic compound was prepared from 30 g of butenyl γ -bromide and 5.3 g of magnesium in 60 ml of ether. The ether was distilled off at $< 90^\circ$, and 36 g of 5-chloro-5-butylnonane was added drop by drop during 5 hr at 70-80°, and the mixture was left overnight. It was then subjected to the usual treatment, and the ether layer was dried with Na_2SO_4 . The ether was then distilled off, and the residue was vacuum distilled. The sole product was that of elimination of HBr from the bromide, viz., 5-butylnon-4-ene, b.p. 91-93° at 10 mm, n_D^{20} 1.4398. Under the same conditions butyl bromide and 5-chloro-5-butylnonane give tetrabutylmethane, in 15% yield.

Raman spectrum analyses were performed by M. I. Batuev.

SUMMARY

1. It has been shown that primary, secondary, and tertiary γ -halides (4-bromobut-1-ene, 4-bromopent-1-ene, and 4-bromo-4-methylpent-1-ene) do not enter into the Grignard-Wurtz reaction, as the introduction of a double bond in the γ -position, similarly to its introduction in the α -position to the halogen atom, greatly lowers the reactivity of the halides, as compared with that of the corresponding saturated alkyl halides; introduction of a double bond in the β -position, on the contrary, enhances reactivity.

2. It is shown that the earlier observed reaction of condensation of $n-C_7H_{15}MgBr$ with tertiary γ -halide (4-bromo-4-propylhepta-1,6-diene) depended on isomerization of one of the allyl radicals of this halide to a propenyl radical, followed by an allyl rearrangement leading to formation of the corresponding secondary halide (6-bromo-4-propylhepta-1,4-diene).

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RESEARCHES ON ACETYLENIC ALCOHOLS AND GLYCOLS

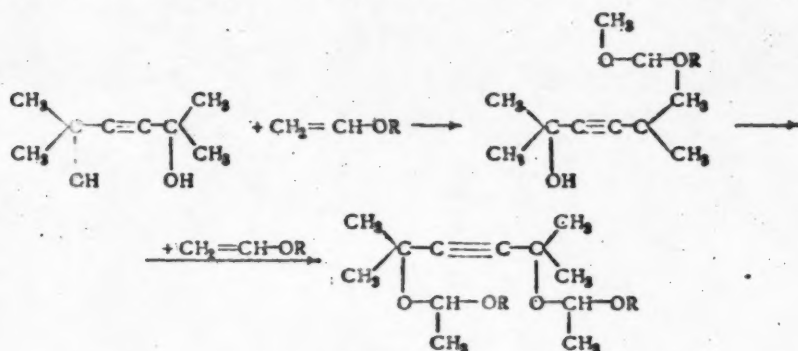
PART 2. SYNTHESIS OF MONO- AND DI-ACETALS OF TETRAMETHYLBUTINDIOL

M. F. Shostakovsky and A. V. Bogdanova

The present paper is a continuation of a study of acetylenic alcohols and glycols, which was initiated with propargyl alcohol, butindiol, and vinyl ethers, and was extended to tetramethylbutindiol.

Tetramethylbutindiol was studied by Zalkind [1], who investigated its hydrogenation with various catalysts, as well as reactions of addition to its triple bond of phenol [2], and of methanol and acetic acid in presence of HgO and BF₃ [3]. Dehydration of the products of addition of phenol and alcohols gives cyclic products of the furan series. Of the reactions of substitution of hydrogen of the hydroxyl groups of tetramethylbutindiol only that with alcohols was studied, leading to formation of tetramethylbutindiol ethers [4,5]. In connection with this, the preparation of new substitution products of tetramethylbutindiol was thought to be of interest.

The synthesis of mono- and di-acetals of tetramethylbutindiol adds considerably to our knowledge of compounds of this type, and by varying the nature of the acetyleneglycol, on the one hand, and of the vinyl ethers on the other, it affords us the opportunity of obtaining different products having a wide range of physical and chemical properties. The reaction of tetramethylbutindiol with vinyl ethers proceeds as follows:



The mono- and di-acetals of tetramethylbutindiol which are formed are of interest for the study of the mechanism of decomposition of substances of this class, due to thermal and other factors. The present paper describes catalytic and thermal methods for the synthesis of acetals of tetramethylbutindiol [6]. The reaction proceeds smoothly, giving good yields of acetals. Certain experimental difficulties were encountered in the process of isolating certain of the monoacetals by repeated vacuum distillation, owing to their instability; thus we could not isolate the monoethyl and monoctyl acetals of tetramethylbutindiol altogether free of saturated products. Our experiments showed that both the catalytic and the thermal methods of synthesis give both mono- and di-acetals depending on the temperature and duration of reaction, and on the amount of catalyst taken. The reaction may be interrupted at the stage of monoacetal production even when excess of vinyl ether is present.

The structure of the acetals was established by a study of their hydrolysis products. In view of the differences in the velocity of hydrolysis of different acetals, the conditions of hydrolysis [6] were varied accordingly (sealed tube, temperature, duration, concentration of acid).

EXPERIMENTAL

Reagents used. Tetramethylbutindiol was prepared by Shkhiyev by Babayan's modification [8] of

* Senior Laboratory Technician M. S. Egorova took part in the work.

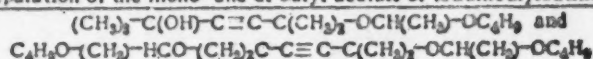
Favorsky's method [7] from acetone and acetylene. After purification it boiled at 121-123° at 7 mm, and melted at 94.5-95.5°. The vinyl ethers were purified by means of the procedure recommended by the Laboratory of Vinyl Compounds [9]; they had the following constants:

Vinyl butyl ether; b.p. 93-94°, n_D^{20} 1.4020.

Vinyl ethyl ether; b.p. 36-36.5°, n_D^{20} 1.3775.

Vinyl octyl ether; b.p. 59-60° at 10 mm, n_D^{20} 1.4275.

Preparation of the mono- and di-butyl acetals of tetramethylbutindiol



1. In an autoclave, 35.5 g (0.25 mole) of crystalline tetramethylbutindiol and 50.0 g of vinyl butyl ether (0.5 mole) were heated in a 1 liter rotating autoclave for 9 hrs at 96-110°, to give 83 g of a clear liquid product, vacuum distillation of which gave:

Fraction I, b.p. up to 76° at 17 mm; 16.0 g

Fraction II, b.p. 76-136° at 14 mm; 22.2 g

Fraction III, b.p. 136-164° at 14 mm; 32.4 g

Residue 7.5 g

Fraction I was vinyl-butyl ether, b.p. 93-94°, n_D^{20} 1.4020.

Fraction II deposited 5.6 g of crystalline tetramethylbutindiol, m.p. 92-94°.

The residue of Fraction II and Fraction III gave two products, one of which had b.p. 121-122° at 7 mm, n_D^{20} 1.4440; d_4^{20} 0.9175; found MR_D 69.93; calculated for $C_{14}H_{26}O_3$ MR_D 69.60.

Found %: C 69.73; 69.51; H 10.77, 10.80

$C_{14}H_{26}O_3$ Calculated %: C 69.40; H 10.82

Found M: 249.8; 247.3 (cryoscopically, in benzene)

$C_{14}H_{26}O_3$ Calculated M: 242.35

Hydrolysis and determination of acetal*

% Acetal found: 96.68, 96.23.

The product was the monobutyl acetal of tetramethylbutindiol; yield 58.8%.

The second product (12 g) had the following constants: b.p. 146-147° at 8 mm, n_D^{20} 1.4380; d_4^{20} 0.9150; found MR_D 98.26; calculated for $C_{21}H_{38}O_4$ MR_D 99.06.

Found %: C 70.25; 70.37; H 11.28; 11.19

$C_{21}H_{38}O_4$ Calculated %: C 70.13; H 11.18

Hydrolysis and determination of acetal

% Ether found: 96.25, 96.54.

The product was the dibutyl acetal of tetramethylbutindiol; yield 16.6%.

2. Catalytic method. A solution of 35.5 g (0.25 mole) of tetramethylbutindiol in 50.0 g of dioxan was placed in a flask fitted with a stirrer, a thermometer, a reflux condenser, and a dropping-funnel, and 50 g (0.5 mole) of vinyl butyl ether was added drop by drop during an hour, as well as 3 drops of concentrated sulfuric acid, the temperature being maintained at 53-56°. The mixture was then heated at 65-70° for 3.5 hrs, after which it was dried over potash. It was then filtered, the filtrate was distilled, giving 56.3 g of dioxan with some vinyl butyl ether, and the residue was vacuum distilled:

Fraction I, b.p. 73-132° at 8 mm; 41 g

Fraction II, b.p. 132-154° at 8 mm; 16.3 g

Residue 7.6 g

10 g of vinyl butyl ether was collected in a cooled receiver, and 1 g of crystalline tetramethylbutindiol was

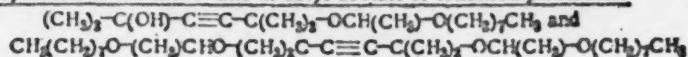
* Hydrolysis was effected by heating a weighed sample in a sealed tube with 25 ml of 0.5 N H_2SO_4 .

separated from Fraction I.

The mono- and di-butyl acetals of tetramethylbutindiol were isolated from the liquid residues of Fractions I and II. The monobutyl acetal had b.p. 122-123° at 7 mm; n_D^{20} 1.4438; d_4^{20} 0.9170; yield 50 g. (84.9%) and the dibutyl acetal had b.p. 147-148° at 7 mm, n_D^{20} 1.4380; d_4^{20} 0.9158; yield 2.4%.

3. The dibutyl acetal of tetramethylbutindiol was prepared as described in 2 above, taking the same amounts of reagents, and under the same conditions, with the difference that the duration of reaction was increased to 8 hrs. The product, yield 66%, boiled at 143-144° at 4 mm, n_D^{20} 1.4375; d_4^{20} 0.9148.

Synthesis of the mono- and di-octyl acetals of tetramethylbutindiol



42 g of vinyl octyl ether was added drop by drop to a solution of 18.5 g of tetramethylbutindiol in 25 g of dioxan containing 4 drops of hydrochloric acid, and the mixture was heated at 75-80° for 6 hrs. The product was treated with potash, and vacuum distilled, giving:

Fraction I, b.p. 25-124° at 36 mm:	23.7 g.
Fraction II, b.p. 124-153° at 11 mm:	3.5 g.
Fraction III, b.p. 153-183° at 11-3 mm:	32.8 g.
Fraction IV, b.p. 183-187° at 3 mm:	18.0 g.
Residue	3.4 g.

Fraction I was dioxan, b.p. 101-101.5°, m.p. 10°. Fraction II deposited 1.0 g of tetramethylbutindiol, m.p. 93-94° (from ethanol Fraction III gave, after repeated redistillation, 21.5 g of a liquid product, having the following constants: b.p. 138-138.2° at 3 mm, n_D^{20} 1.4420; d_4^{20} 0.8713; found MR_D 90.64; calculated for $C_{18}H_{34}O_3$ MR_D 88.97.

Found M: 282.2; 287.4 (cryoscopic, in benzene)
 $C_{18}H_{34}O_3$. Calculated M: 298.45

Hydrolysis and determination of acetal

% Acetal found: 92.38

The Fraction contains 92.38% of the monocetyl acetal of tetramethylbutindiol, which was thus obtained in 62.0% yield.

16 g of a product having the following constants was isolated from Fraction IV: b.p. 184-186° at 1 mm, n_D^{20} 1.4460; d_4^{20} 0.8905; found MR_D 136.2; calculated for $C_{28}H_{54}O_4$ MR_D 136.01.

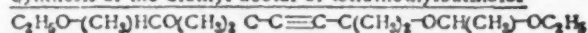
Found %: C 74.02; 73.80; H 11.62; 11.90
 $C_{28}H_{54}O_3$. Calculated %: C 73.96; H 11.97
Found M: 450.0; 436.2 (cryoscopic, in benzene)
 $C_{28}H_{54}O_4$. Calculated M: 454.71

Hydrolysis and determination of acetal

% Acetal found: 94.91, 95.14.

This product is the dioctyl acetal of tetramethylbutindiol, yield 30.3%.

Synthesis of the diethyl acetal of tetramethylbutindiol



36.0 g (0.5 mole) of vinyl ethyl ether was added, under similar conditions to those described above, to a solution of 35.5 g (0.25 mole) of tetramethylbutindiol in 50 g of dioxan at 43-45°, in presence of 4 drops of hydrochloric acid. After heating at 65-70° for 5 hrs the dioxan was distilled off, and the residue was vacuum-distilled:

Fraction I, b.p. 110-120° at 9 mm:	11.5 g
Fraction II, b.p. 120-132° at 9 mm:	44.5 g
Residue	10.0 g

Fractions I and II were redistilled, giving 40 g of a product having the following constants: b.p. 103.5-105° at 2 mm, n_D^{20} 1.4320; d_4^{20} 0.9125; found M_R 81.41; calculated for $C_{16}H_{32}O_4$ M_R 80.6.

	Found %:	C 67.44; 67.54,	H 10.49; 10.38
$C_{16}H_{32}O_4$	Calculated %:	C 67.11;	H 10.58
	Found M:	280.8; 258.0	(cryoscopic, in benzene)
$C_{16}H_{32}O_4$	Calculated M:	286.4	

Hydrolysis and determination of acetal

% Acetal found: 93.28, 94.37

The product was the diethyl acetal of tetramethylbutindiol; yield 56.0%.

SUMMARY

1. A study has been made of the reactions of tetramethylbutindiol with vinyl ethyl, butyl, and octyl ether, leading to production of mono- and di-acetals of tetramethylbutindiol, in yields of up to 85%.
2. Five new acetals were thus prepared, and their structure was established by a study of their hydrolysis products.
3. The diacetals are formed through the intermediate stage of mono-acetals, the yield of which depends on the amount of vinyl ethers taken for the reaction, and on its duration.

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* See Consultants Bureau English Translation, p. 923.

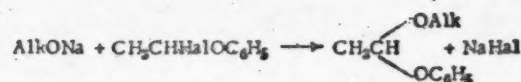
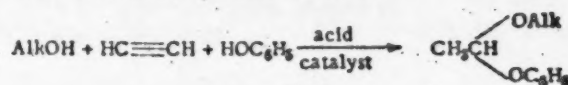
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INDIRECT VINYLATION OF ALIPHATIC ALCOHOLS

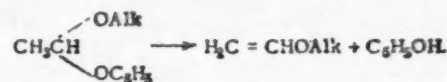
M. F. Shostakovsky, B. I. Mikhantsev, and N. N. Ovchinnikova

Direct vinylation with acetylene of primary and secondary C_1-C_4 alcohols proceeds smoothly at $140-160^\circ$ in presence of KOH, giving yields of up to 95% of the corresponding ethers [1]. Tertiary alcohols and alcohols with double or triple bonds do not react with acetylene under the same conditions. The vinylation of tertiary, and more particularly of unsaturated, aliphatic alcohols is of considerable theoretical and practical interest.

The proposed indirect method for vinylation of tertiary and ethylenic aliphatic alcohols follows directly from the researches of Shostakovsky [2] and his co-workers in the Laboratory of Vinyl Compounds, who found that alcohols or alkoxides or alkaline solutions of alcohols react with vinyl phenyl or α -halogenoethyl phenyl ethers to give mixed alkyl phenyl acetals, as follows:

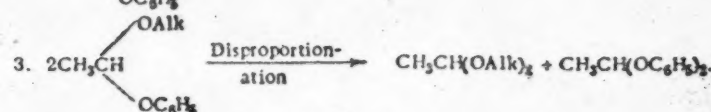
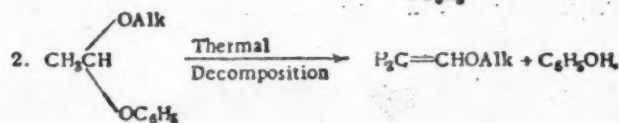
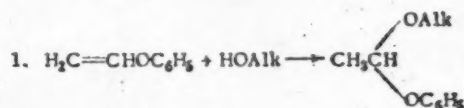


The formation of vinyl alkyl ethers by the thermal decomposition of alkyl phenyl acetals was shown to take place [2], as follows:



The reaction was also confirmed by the work of other authors [3], who ascribed the decomposition of the acetals to the catalytic action of inorganic acids or their salts, and of sulfanilic acid or anilsulfate. The yields of vinyl ethers so obtained varied from 50-74%.

The reagents used in our research were vinyl phenyl ether and secondary and tertiary butyl and allyl alcohols, from which we synthesized the corresponding mixed acetals, heating of which on an air-bath in all cases led to decomposition of the acetals, with formation of the vinyl ether of the given alcohol, together with phenol. Vacuum distillation of the mixed alcohols at pressures of 25-35 mm gave rise to alkyl vinyl ethers, dialkyl acetals, diphenyl acetal, and phenol. Distillation at 3-5 mm pressure gave only disproportionation products. The transformations observed may be represented by the following reactions:



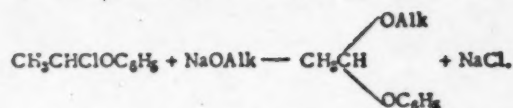
where Alk is secondary or tertiary butyl or allyl.

It appears from the above reaction schemes that aryl alkyl acetals are the starting point for the preparation not only of the corresponding symmetrical acetals [4-5] but also of vinyl ethers of secondary and tertiary alcohols and unsaturated alcohols.

TABLE 1 Specification of initial reagents

Compound	b.p. °C/760 mm	n_D^{20}	d_4^{20}	Remarks
sec.-Butanol $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$	97-93	1.3952	0.8075	
tert.-Butanol $(\text{CH}_3)_3\text{COH}$	82.5	—	—	m.p. 25.3° n_D^{20} 1.3824 d_4^{20} 0.7775
Allyl alcohol $\text{CH}_2=\text{CHCH}_2\text{OH}$	96-97	1.4132	0.8550	
Vinyl phenyl ether $\text{CH}_2=\text{CHOC}_6\text{H}_5$	155-156	1.5224	0.9768	
α -Chloroethyl phenyl ether $\text{CH}_3\text{CHClOC}_6\text{H}_5$		1.5225	1.1150	b.p. 93-94/22 mm

readily available α -chloroethyl phenyl ether [6] and the appropriate alkoxides, by the reaction:



Vacuum distillation of the reaction mixture gave up to 40% yields of aryl alkyl acetals, which were further treated as above, i.e., the mixed acetals were decomposed to give vinyl alkyl ether and phenol, or disproportionated to give the symmetrical acetals.

EXPERIMENTAL

The aryl alkyl acetals were prepared in a flask fitted with a stirrer, a thermometer, and a reflux condenser, the temperature being regulated by a water-bath. An example of a synthesis is given below. The physical constants of the reagents used are given in Table 1.

tert.-Butyl phenyl acetal. 0.2 g of P_2O_5 catalyst (or concentrated H_2SO_4 or HCl) was added to a mixture of 37 g of tert.-butanol (0.5 mole) and 60 g of vinyl phenyl ether (0.5 mole) at 30°. The temperature rose to 75-80° after 30 minutes, and the mixture turned faint yellow. After it had cooled to room temperature the mixture was treated with potash and with sodium, and then vacuum-distilled. Redistillation of the fractions obtained gave the following individual products:

tert.-Butyl phenyl acetal	26.2 g (27% yield)
Di-tert.-butyl acetal	12.2 g (28% yield)
Diphenyl acetal	13.4 g (25% yield)

Hydrolysis of tert.-butyl phenyl acetal, and determination of its percentage content*

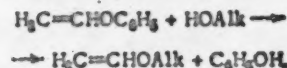
30.9 ml of 0.1 N- I_2 was used to titrate 25 ml of bisulfate % Acetal found: 95.55, 96.11

25 g of tert.-butyl phenyl acetal (see Table 2 for physical constants) was heated in a Favorsky flask fitted with a thermometer, and connected with an upright condenser, on an air-bath at 140-150°, giving vinyl tert.-butyl ether (9.63 g., or 75% yield) and phenol (6 g isolated from the tarry residue).

Allyl phenyl acetal. 40 g of sodium allyloxide (0.5 mole) was placed in a flask, and 78.3 g (0.5 mole) of α -chloroethyl phenyl ether was added drop by drop during 1 hour. The temperature of the mixture rose to 62°, and its color darkened. Solid products were filtered off and discarded, and the filtrate was distilled at 3 mm, giving the following products:

* Hydrolysis was effected by heating weighed samples of the acetals in a sealed tube with 25 ml of 0.5N- H_2SO_4 .

Acetal formation took place at temperatures 2-3°, lower than the boiling point of the corresponding vinyl alkyl ether, as this gave the highest yields of mixed acetals (25-32%). Vinyl alkyl ethers are obtained in yields of up to 77%. The reaction of indirect vinylation amounts to transesterification of aryl radicals of vinyl aryl ethers by alkyl radicals, as follows:



which is of special importance in the case of unsaturated alcohols, direct vinylation of which has not yet been achieved.

In order to raise the yield of aryl alkyl acetals we prepared them from

TABLE 2

Characteristics of the acetals obtained

Compound	Yield %	B.p. °C	Pressure mm	d_4^{20}	n_D^{20}	M_r found, calc.	M found calc.	% C found calc.	% H found calc.
sec.-Butyl phenyl acetal* $\begin{array}{c} \text{OCHCH}_2\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3\text{CH} \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{OC}_6\text{H}_5 \end{array}$	32-40	57-60	5	0.9552	1.4786	57.308 57.481	193.02 194.264	74.02 74.19	9.36 9.34
Di-sec.-butyl acetal* $\begin{array}{c} \text{OCHCH}_2\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3\text{CH} \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{OC}_6\text{H}_5 \end{array}$	27-35	73-74	25	0.8231	1.4048	51.548 51.886	173.18 174.276	68.94 68.91	12.68 12.72
tert.-Butyl phenyl acetal* $\begin{array}{c} \text{OC}(\text{CH}_3)_3 \\ \diagup \quad \diagdown \\ \text{CH}_3\text{CH} \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{OC}_6\text{H}_5 \end{array}$	27-36	53-55	5	0.9560	1.4790	57.839 57.481	195.00 194.264	74.28 74.19	9.17 9.34
Di-tert.-butyl acetal $\text{CH}_3\text{CH}[\text{OC}(\text{CH}_3)_3]_2$	28-31	63-64	13	0.8246	1.4054	51.685 51.886	174.30 174.276	68.74 68.91	12.85 12.72
Allyl phenyl acetal* $\begin{array}{c} \text{OCH}_2\text{CH}=\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CH} \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{OC}_6\text{H}_5 \end{array}$	25-30	65-67	8	0.9613	1.4908	51.547 52.356	178.35 178.222	74.14 74.13	7.82 7.92
Diallyl acetal $\text{CH}_3\text{CH}[\text{OCH}_2\text{CH}=\text{CH}_2]_2$	22-26	147-149	760	0.8482	1.4208	42.138 41.636	141.98 142.192	67.58 67.57	9.76 9.92
Diphenyl acetal** $\text{CH}_3\text{CH}(\text{OC}_6\text{H}_5)_2$	25-23	144-146	35	1.0805	1.5542	64.009 63.076	216.03 214.252	78.44 78.48	6.87 6.59

* Not previously prepared.

** Diphenyl acetal was obtained by the disproportionation of all three aryl alkyl acetals. In Table 2 we give data relating to diphenyl acetal obtained from allyl phenyl acetal.

*** In the column "Yield %" the first figure refers to the yield of products obtained by the reaction of vinyl phenyl ethers with alcohols, and the second to acetals obtained from alkoxides and chloro-ether.

Allyl phenyl acetal

27 g (30% yield)

Diallyl acetal

9.2 g (26% yield)

Diphenyl acetal

12.3 g (23% yield)

Hydrolysis of allyl phenyl acetal, and determination of its percentage content
 31.2 ml of 0.1 N- I_2 was used to titrate 25 ml of bisulfite % Acetal found: 95.97, 98.27.

Decomposition of 27 g of allyl phenyl acetal gave 9.81 g of vinyl allyl ether (77% yield). Analytical data and physical constants of the compounds obtained are given in Tables 2 and 3; the physical constants agree

TABLE 3

Characteristics of the vinyl alkyl ethers obtained

Compound	Yield (%)	B.p. °C/760 mm.	d_4^{20}	n_D^{20}	MR _D found, calc.	M found, calc.	%C found, calc.	%H found, calc.
Vinyl sec.-butyl ether $H_2C=CHOC(CH_3)CH_2CH_3$	75.8	81-81.5	0.7720	1.3970	31.397 31.204	100.65 100.156	72.01 71.95	12.03 12.08
Vinyl tert-butyl ether $H_2C=CHOC(CH_3)_3$	75.0	75-75.3	0.7726	1.3978	31.308 31.204	100.27 100.156	71.85 71.95	12.41 12.08
Vinyl allyl ether $H_2C=CHOCCH_2CH=CH_2$	77.0	66-66.7	0.7900	1.4062	26.219 26.079	84.29 84.124	71.53 71.39	9.44 9.59

closely with those quoted in the literature [7]. The structure of the three new aryl alkyl acetals was also established by hydrolysis.

A comparison of the two methods of preparation of aryl alkyl acetals, from alcohols and vinyl phenyl ethers, and from alkoxides and α -chloroethyl phenyl ether, shows that the latter method gives somewhat higher yields (36%, as compared with 27% of tert.-butyl phenyl acetal by the former method).

SUMMARY

1. A method has been worked out for the indirect vinylation of tertiary and unsaturated aliphatic alcohols.
2. sec.-Butyl phenyl acetal, tert.-butyl phenyl acetal, and allyl phenyl acetal have been synthesized; they have not previously been described.

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* See Consultants Bureau English Translation, p. 643.

** See Consultants Bureau English Translation, p. 1379.

METALLO-ORGANIC "BIURET" COMPLEXES OF PROTEIN BREAKDOWN PRODUCTS

K. T. Poroshin

The study of the processes and products of breakdown of proteins is attracting ever increasing attention. Among the publications of numerous authors who have worked on this subject, the most important are those of Zelinsky and Sadikov [1], Perov [2], Reznichenko [3], and Blagoveshchensky [4]. Work on the problems of breakdown of natural and synthetic high-molecular compounds other than proteins has been done by Korshak and co-workers [5] (polyamides and polyesters), Ivanov, Kaverzneva, and Golova [6] (cellulose), and Knunyants and Rogovin [7] (polycaprolactam).

Among the many methods applicable to the study of processes and products of protein degradation, that depending on the investigation of metallo-organic "biuret" complexes may be of considerable value. The researches of Gavrilov et al., and our own work [8], have opened up promising prospects for the further study of the structure of protein macromolecules. The present paper describes the results of a spectrophotometric study of solutions of copper "biuret" complexes of protein degradation products. The products studied were peptones ("Witte", "Farmakon", and "Siegfried"), and hydrolyzate-peptones from legumin and glycinin, as well as for two protein derivatives of the "proto-acid" type.

Hydrolyzate-peptones from proto-acids, legumin, and glycinin were prepared by hydrolysis with 0.1% hydrochloric acid, by the method described by the authors [9]. The proteins (proto-acids) taken have already been the subjects of detailed chemical and physico-chemical studies [10]. The copper "biuret" complexes were prepared as follows. 3% Caustic soda was added to 100 mg of peptone or hydrolyzate-peptone in amount sufficient to dissolve it, and the volume was made up to 100 ml. 0.25 M Copper acetate was then added until a permanent precipitate of hydroxide separated. The solution was centrifuged after 1-2 hours, and the intensity of coloration of the supernatant fluid was measured by means of a Koenig-Martens spectrophotometer. The results obtained for copper "biuret" complexes of peptones are given in Table 1.

The spectrophotometric absorption curves are given in Fig. 1; it may be concluded from an analysis of the data of Table 1 and Fig. 1 that the various peptones have different absorption maxima, and that the absorption curves are of different types. The absorption maxima are at 530 m μ for Siegfried peptone, at 540 m μ for Witte's peptone, and at 550 m μ for "Farmakon" peptone. The magnitude of absorption for Witte's peptone differs from that for the other two. The spectrophotometric results thus reveal differences in the structures of the three peptones.

The results obtained similarly are shown in Table 2 and Fig. 2, from which it appears that the curves obtained for proto-acid peptones are of the same type, with absorption maxima at 550 m μ . Only small differences in intensity of absorption are found, the greatest difference, at 505-530 m μ , not exceeding 0.0111.

A somewhat different picture is observed with the hydrolyzate-peptones from legumin and glycinin. Solutions of the "biuret" complex from legumin or glycinin have absorption maxima at 540 and 550 m μ , respectively, and the shape of the curves differs. At certain wavelengths a difference in the intensity of absorption is observed, as compared with proto-acid preparations. It is evident that the hydrolyzate-peptones from proto-acid proteins are more homogeneous than are those from legumin and glycinin.

Our experiments show that various forms of primary degradation of proteins, such as enzymatic (pepsin)

TABLE 1

Values of absorption of light ϵ for solutions of copper "biuret" complexes of peptones

Wave-length m μ	"Siegfried" peptone	"Farmakon" peptone	"Witte's" peptone
480	0.1275	0.1509	0.1567
505	0.2107	0.2109	0.2404
530	0.2612	0.2492	0.2712
540	0.2595	0.2550	0.2793
550	0.2580	0.2603	0.2775
560	0.2469	0.2534	0.2705
580	0.2337	0.2314	0.2527
610	0.1339	0.1915	0.2135
630	0.1597	0.1634	0.1877
690	0.0987	0.0887	0.0987
730	0.0414	0.0503	0.0594

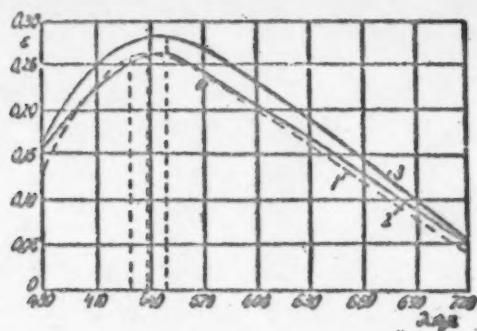


Fig. 1. Spectrophotometric curves for copper "biuret" complexes: 1 - Siegfried peptone; 2 - Farmakon peptone; 3 - Witte's peptone.

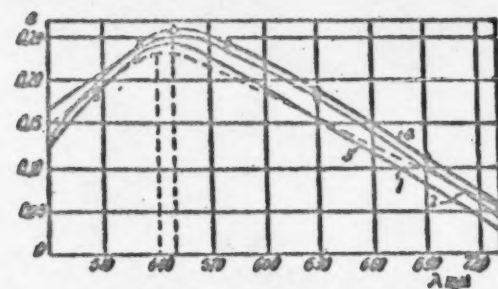


Fig. 2. Spectrophotometric absorption curves for copper "biuret" complexes: 1 - hydrolyzate-peptone from glycine; 2 - hydrolyzate-peptone from casein; 3 - hydrolyzate-peptone from legumin; 4 - hydrolyzate-peptone from pea-seed protein.

TABLE 2

Values of ϵ for solutions of copper "biuret" complexes from protein hydrolyzate-peptones prepared from proteins.

Wave-length mμ	Casein acid hydrolyzate	Pea protein hydroly- zate (proto-acid)	Legumin hydrolyzate	Glycine hydrolyzate
480	0.1263	0.1378	0.1517	0.1648
505	0.1797	0.1908	0.1830	0.2004
530	0.2285	0.2396	0.2205	0.2302
540	0.2417	0.2497	0.2300	0.2372
550	0.2503	0.2572	0.2282	0.2408
560	0.2473	0.2538	0.2204	0.2330
580	0.2331	0.2409	0.2033	0.2129
610	0.2048	0.2112	0.1725	0.1738
630	0.1787	0.1870	0.1527	0.1507
690	0.0994	0.1102	0.0978	0.0905
730	0.0457	0.0608	0.0560	0.0312

TABLE 3

Amount of copper, in mg., needed for the formation of the red complex of casein acid and its hydrolyzates.

Product	Mg of Cu per g of product
1. Casein acid	9.2
2. Hydrolyzate obtained by action of pepsin on casein acid	18.8
3. Hydrolyzate obtained by casein acid with 0.1% HCl	39.2
4. Hydrolyzate obtained by hydrolysis of casein acid with 2% H ₂ SO ₄	56.7

or acid (0.1% HCl, 2% H₂SO₄) hydrolysis, lead to production of compounds giving red copper complexes with an absorption maximum at 550 mμ, as compounds are formed with a longer polyamide (polypeptide) chain than the tripeptide ones existing before hydrolysis. In connection with this we observe a shift of the absorption maximum in the direction of shorter wave-lengths. Thus, for example, if the solution of copper "biuret" complex of casein acid exhibited an absorption maximum of 560 mμ before hydrolysis, this maximum was shifted to 550 mμ after degradation of the protein. The amount of peptides in the primary degradation products may be determined by means of the method of differentiated spectrophotometry developed by us [8]. It may be expressed quantitatively as milligrams of copper bound in the red "biuret" complex, and the figures of Table 3 express the variations found in this value in different forms of degradation of the protein.

As has been shown earlier [10], the protein macromolecule consists basically of tripeptides, which make up 92% of the molecule. The amount of peptides giving a red "biuret" complex with copper increases during the early stages of protein degradation. This effect cannot be explained on the basis of a protein macromolecule structure involving only peptides.

SUMMARY

1. The absorption curves of solutions of copper "biuret" complexes of primary degradation products of a number of proteins have been constructed.

2. It is shown that the copper "biuret" complexes derived from proteins of the "proto-acid" type have identical absorption maxima, and equal intensity of absorption.

3. Red copper "biuret" complexes are given by the polypeptides (polyamides) formed during the initial period of primary protein degradation.

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HIGH-MOLECULAR COMPOUNDS

PART 52. REACTIONS OF POLYESTER MACROMOLECULES WITH EACH OTHER

V. V. Korshak and S. V. Vinogradova

The presence of exchange reactions in the process of polycondensation is one of the most characteristic features of reactions of this type [1]. The laws governing the reactions of ester bonds were studied by us, for the case of reaction of low-molecular esters with acids, alcohols, and other esters [2,3,4,5]. The presence of exchange reactions between polyesters and low-molecular alcohols, leading to degradation of the polyester, was demonstrated by us for the reaction between polyhexamethylene sebacate and cetyl alcohol [6]. The reaction of alcoholysis of polyesters has been demonstrated earlier by Flory [7], who did not, however, include this among the series of degradative reactions. Reactions of polyesters with dicarboxylic acid and glycols, involving their degradation, were first shown by one of us together with Golubev [8]. Similar degradative reactions of polyamides with dicarboxylic acids or diamines have been reported much earlier by one of us together with Rafikov [9] and Zamyatina [10].

All these examples, however, related to the reaction of polyesters or polyamides with low-molecular compounds, such as mono- or di-carboxylic acids, or glycols, alcohols, diamines, and other such compounds, which enter, as was shown by us in the study of the kinetics of the reactions of hexamethyleneglycol with sebacic acid [11], only into the initial stages of the polycondensation process, i.e., at the stage at which the polycondensation products are still of low molecular weight. As the process continues these low molecular weight initial products are used up, and the role played by such compounds diminishes correspondingly. It might hence be supposed that the role of degradative reactions should diminish in the terminal stages of polycondensation reactions, but this supposition is contradicted by the finding that the differential curve of distribution of polyamides according to their molecular weights exhibits a sharp maximum, as was shown by one of us with Zamyatina [12]. The presence of a maximum was found by one of us together with Rafikov and Chelnokova for the differential distribution of polyesters according to their molecular weights [13]. These results are in disagreement with Flory's theory [14], and are ascribable to the existence of degradative exchange reactions at all stages of the polycondensation process [12,13]. It follows that the activity of the macromolecules formed at all stages of the polycondensation process is fairly high, in spite of their comparatively high molecular weight.

The high reactivity of macromolecules in the reaction of chain growth was established by us on the basis of a study of the reaction of polycondensation of hexamethyleneglycol with sebacic acid [11]. We found that the growth of the chains in the terminal stages of the polycondensation reaction is due exclusively to reactions between polyester macromolecules. We thought it would be of considerable interest to elucidate the role and significance of exchange, chiefly degradative, reactions in the terminal stages of polycondensation reactions, at which the original substrates are practically absent, so that the reactions can only be between condensation products. With this object we subjected the reaction between two polyesters of different molecular weight, derived from hexamethyleneglycol and sebacic acid.

EXPERIMENTAL

Initial reagents. The initial polyesters were derived from sebacic acid and hexamethyleneglycol. The reaction was conducted by heating the substrates in a stream of nitrogen from which oxygen had been eliminated by passing over a heated copper spiral. The reaction mixture was heated for 4 hrs at 180° and then for 4 hrs at 190-195°, followed by 3 hrs at 225°. It was then heated in vacuum (2 mm) for 30 hrs, during which the temperature was gradually raised to 250°. Two polyesters were obtained: polyester No. 1, from equivalent amounts of acid and glycol, with a molecular weight of 6608, as derived from viscosity measurements of its benzene solution, and polyester No. 2, obtained with a 30% excess of hexamethyleneglycol, molecular weight 1533 (from viscosity of 0.5% benzene solution).

Experimental results. We first performed preliminary experiments on the effect of temperature on the polyesters, in order to be able to select temperatures at which the reaction velocity was high enough for our purposes, but at which thermal degradation of the polyesters did not take place. For this purpose we examined the effect of heating different polyesters at various temperatures for 10 hrs.

Weighed portions of polyesters were placed in tubes, from which the air was then swept with nitrogen, and the tube was evacuated and sealed, and placed in a thermostat, where it was left for 10 hrs at the appropriate temperature. The results are given in Table 1. The initial molecular weight of the polyester, as determined from viscosity of benzene solutions, was 9540. The data given in Table 1 show that considerable degradation takes place during heating, to an extent proportional to the temperature.

TABLE 1

Thermal degradation of polyesters

Temperature °C	100	150	180	200	250
Molecular weight, from viscosity measurements	9540	8170	7500	6820	6130

6810 to 5500, under the same conditions, a difference of only 19%, and a third from 3270 to 2840, or only 13%. A polyester of molecular weight 6600 was practically unchanged after 35 hrs at 150°, and this temperature was therefore taken as the optimum one for our experiments.

We next determined the time needed for attainment of equilibrium at this temperature. A tube was filled with a mixture of equal weights of polyesters of molecular weights 6608 and 1533, and the viscosity of benzene solutions of the product after various times 150° was determined, as well as the content of terminal groups (OH and COOH); the molecular weights of the products were hence determined. Terminal groups were determined by the method described in an earlier paper [15]. The results are given in Table 2.

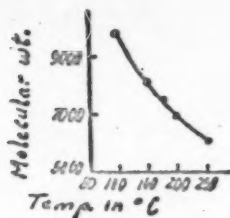


Fig. 1. Thermal degradation of polyester.

TABLE 2

Kinetics of reaction of two polyesters

Serial No.	Duration of heating, hr.	Viscosity of 0.5% solution in benzene	Molecular weight, from viscosity	M ⁿ of 0.02 N NaOH used per g of polyester	Molecular weight, from terminal group determination	Polydispersity coefficient M_w/M_n
1	0.0	0.119	4054	47.6	2100	1.93
2	3.0	0.110	3747	47.6	2100	1.78
3	6.0	0.102	3475	47.6	2100	1.68
4	9.0	0.097	3303	47.6	2100	1.57
5	14.0	0.078	2657	47.5	2100	1.26
6	20.0	0.078	2657	47.6	2100	1.26
7	35.0	0.076	2589	47.6	2100	1.23

Note: Molecular weight was calculated from terminal group content by the formula $M = \frac{100,000}{a}$, where a is ml of 0.02 N NaOH used per g of polyester.

The curve of Fig. 1 shows the connection between temperature and extent of degradation.

The depth of thermal degradation also depended on the molecular weight of the initial polyester. Thus the molecular weight of a polyester fell from 9540 to 6130, i.e., by 36% after 10 hr of heating at 250°, whereas that of a second polyester fell from

It appears from the data of Table 2 that equilibrium is practically achieved after 14 hrs of heating, after which very little further change in molecular weight takes place even after a further 20 hrs. Having thus established the possibility of achieving an equilibrium state of the exchange reaction between the two polyesters, we studied this reaction as a process of degradation of the higher molecular weight polyester No. 1 (M 6608) by the lower molecular weight ester No. 2 (M 1533). The ratio of the initial polyesters taken was such that 0.5 to 100% of polyester No. 2 was taken per part by weight of polyester No. 1. The properties of a range of such mixtures were determined before heating, and are recorded in Table 3.

TABLE 3

Properties of mixtures of polyesters

Amount of low molecular weight polyester, as % by wt.	Specific viscosity of a 0.5% solution in benzene	Molecular weight, from viscosity M_v	Ml 0.02 N alkali used in titration of terminal groups	Molecular weight, from terminal groups, M_t	Polydispersity coefficient M_v/M_t
0.0	0.194	6608	15.2	6579	1.004
0.5	0.193	6575	15.9	6289	1.04
3.0	0.190	6473	17.0	5882	1.10
7.5	0.183	6234	19.7	5076	1.22
15.0	0.174	5978	23.8	4223	1.42
25.0	0.164	5587	28.1	3558	1.57
50.0	0.145	4940	38.8	2577	1.66
75.0	0.130	4429	41.6	2403	1.84
100.0	0.120	4088	47.6	2100	1.95

The data of Table 3 confirm the previously expressed view that the polydispersity coefficient, which is the ratio of the molecular weights as derived from viscosity and terminal group determinations, respectively, may provide us with a useful measure of the polydispersity of the given polymer. As appears from Table 3, the polydispersity coefficient rises sharply with increase in the polydispersity of the given mixture. Fig. 2 shows graphically how the two molecular weights vary according to the content of one or the other polyester in the mixtures.

The mixtures were placed in tubes and heated for 35 hrs at 150° in an atmosphere of nitrogen. The tubes were allowed to cool, and were then opened and the contents were examined; the results are given in Table 4.

TABLE 4

Degradation of high-molecular polyester by the action of low-molecular polyester

Amount of low-molecular weight polyester, as % by wt.	Specific viscosity of a 0.5% solution in benzene	Molecular weight, from viscosity M_v	Ml 0.02 N alkali used in titration of terminal groups	Molecular weight, from terminal groups M_t	Calculated molecular weight	Polydispersity coefficient M_v/M_t
0.0	0.194	6608	15.2	6579	—	—
0.5	0.166	5655	15.9	6289	6439	0.9
3.0	0.160	5451	17.1	5882	5854	0.92
7.5	0.144	4906	19.7	5076	5077	0.96
15.0	0.118	4360	23.7	4223	4280	1.03
25.0	0.115	3918	28.2	3558	3550	1.10
50.0	0.091	3100	38.8	2577	2717	1.20
75.0	0.086	2930	41.5	2403	2323	1.21
100.0	0.076	2589	47.6	2100	2108	1.23

NOTE: Molecular weight was calculated from the formula: $M = \frac{100 + q}{\frac{100}{M_0} - \frac{q}{M_1}}$.

Discussion of results. The experiments show that polyesters of different molecular weights react with each other when heated together, giving products having the mean molecular weight of the mixture. This process resembles that observed when polyesters are heated with dicarboxylic acids, as described by one of us and Golubev [8]. The process is of a degradative nature, as may readily be seen from an inspection of the curves of Fig. 3, plotted from the data of Table 4.

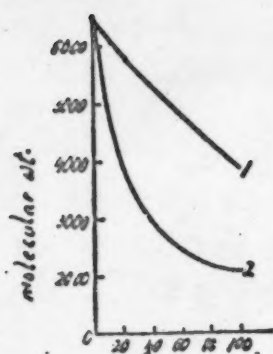


Fig. 2. 1) Change in molecular weight as calculated from viscosity; 2) change in molecular weight as calculated from terminal groups.

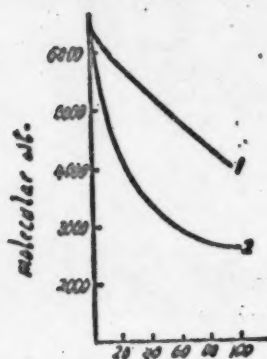


Fig. 3. 1) Change in molecular weight as calculated from viscosity, before heating; 2) change in molecular weight as calculated from viscosity, after heating.

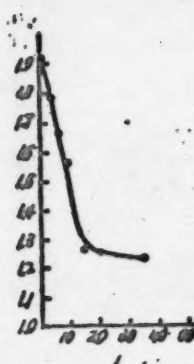


Fig. 4. Change in polydispersity coefficient with time.

We see from Fig. 3 that the fall in molecular weight of a mixture of two polyesters taking place after heating is much greater than would follow from the simple addition rule, showing that reaction must have taken place between the two polyesters. It may thus be concluded that degradation of the high-molecular by the low-molecular polyester does in fact take place. Fig. 4, which represents change in polydispersity coefficient during heating, shows that this reaction is one of degradation, and like all such processes, it leads to increase in homogeneity of the polyester.

As appears from Fig. 4, based on the data of Table 1, heating the polyester mixture leads to lowering of the molecular weight and of the polydispersity coefficient of the product. Similar effects are observed when we heat mixtures containing various proportions of low-molecular polyester, which in this case acts as the degradative agent. Fig. 3, which is based on the data of Table 4, illustrates the relation between change in molecular weight after heating mixtures of polyesters and the content of low-molecular polyester. Whereas Fig. 4 shows the rate of change of polydispersity with time, Fig. 5 represents change in polydispersity of the polyester after achievement of the equilibrium state, i.e., after completion of the degradative process. As appears from Fig. 5, increase in the proportion of the low-molecular polyester favors the degradative process, and so leads to the formation of an increasingly monodisperse polyester.

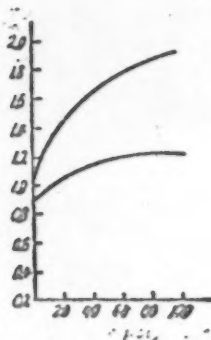


Fig. 5. 1) Change in coefficient of polydispersity of polyester mixture before heating; 2) after heating.

Our results are of importance not only for the comprehension of the individual stages and steps of the process under consideration, but also for the understanding of certain general and basic aspects of the process of polycondensation, in general. An important consequence of this research is the establishment of the presence of exchange reactions proceeding between polyester molecules in the absence of the initial substrates. The existence of these exchange reactions is in the given case demonstrated by the reaction between two polyesters of differing molecular weight, but it should be supposed that it also takes place between polyesters of similar or even identical molecular weight. The present study has thus afforded additional confirmation of the existence of exchange reactions between growing molecules, proceeding without the agency of low-molecular initial substrates. Bearing in mind that the content of terminal groups falls rapidly with growth

of the chains it will be obvious that such exchange reactions may be of importance both when they proceed at the expense of terminal groups and when they depend on reaction between ester bonds of different chains. This possibility has been envisaged by us in an earlier paper [5].

SUMMARY

1. A study of the exchange reaction between polyesters of different molecular weight shows that they react to give a single polyester.
2. The low-molecular polyester acts as a degradative agent with respect to the high-molecular ester.
3. The extent of degradation of the high-molecular polyester is proportional to the content of low-molecular polyester in the mixture.
4. The polydispersity coefficient falls during heating of polyester mixtures as a result of the degradative reaction.
5. A study of the kinetics of degradation of high-molecular polyesters when heated with low-molecular polyesters shows that the polydispersity coefficient falls regularly as the reaction proceeds.
6. A study has been made of the thermal degradation of polyesters at various temperatures.
7. The exchange reaction is shown to be of considerable significance for the process of polycondensation.

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REMARKS ON "THE THEORY OF RESONANCE OR MESOMERISM"

Ya. K. Syrkin and M. E. Dyatkina

That work of genius of I. V. Stalin "Marxism and problems of linguistics" which has brought about a veritable revolution in the domain of linguistics was an outstanding contribution to the theoretical superstructure of Marxism-Leninism. In the same way as over 40 years ago V. I. Lenin, in his work of genius "Materialism and Empirio-criticism", liberated the natural sciences from mysticism and Machism, Comrade Stalin's work on the problems of linguistics led Soviet linguistics out of the critical situation in which it had found itself, and freed it of the vulgarizing and mistaken "new teaching" of the science of language.

Having creatively developed and enriched Marxist-Leninist theory with its new discoveries and propositions, I. V. Stalin's work has pointed the way towards further development and achievement of all domains of Soviet science. At the same time, this work has dealt a decisive blow to idealism, metaphysics, and reactionary ideology. Stalin's memorable words, that "no science can develop and flourish without a clash of ideas, without free criticism" have become the motto of those engaged in creative science. This proposition establishes a new and important dialectic law governing the motive force of our development, which is criticism and self-criticism. Comrade Stalin's work "Marxism and the problems of linguistics" teaches all those who are active in Soviet culture how to apply veritable partisanship to science, this partisanship being diametrically opposed to bourgeois objectivism. At the same time, veritable partisanship in no way rejects a really objective analysis of natural phenomena, inasmuch as really scientific, objective explanations of the laws governing the world of reality are always and in every case found to confirm the correctness of dialectic materialism.

In view of I. V. Stalin's brilliant treatise "Marxism and the problems of linguistics", and of the historic resolutions of the Central Committee of the All-Union Communist Party on the problems of ideological work, we should adopt a critical attitude to the results of our earlier researches, and we should reconstruct our scientific work on the basis of the creative application of Marxist-Leninist theory. The absence of the creative application of the laws of materialistic dialectics to particular domains of knowledge leads to conclusions which are in contradiction to true science, and to pseudo-scientific theories. One example which confirms the truth of this proposition is the profoundly erroneous "resonance theory", which was, to their great regret, for a long time supported by the authors of this paper. A critical survey of our earlier papers connected with the "resonance theory", together with their analysis in the light of Marxist-Leninist teaching, leads us to the conclusion that the reason for our errors was that we did not, in our research work, creatively apply the principles of dialectical materialism, we did not adopt a critical attitude towards the quasi-scientific ideas of the moribund culture of the capitalistic West, and we did not appraise at its true value the progressive significance of the materialistic theory of chemical structure, of which the creator was that classical figure of Russian natural science, A. M. Butlerov.

During the course of the discussions which took place in June 1951 we acknowledged the mistaken nature of the "resonance theory", and the erroneous nature of those of our papers in which we made use of this theory, or supported it. In this connection we consider it to be necessary to dwell on the problems and the role of Russian science in creating the theory of chemical structure, and on the significance of Butlerov's ideas for the whole of the later development which took place in this domain, as well as on the methodological origins of the errors of the "resonance theory", and on the chemical absurdities of this "theory". The basic error of our book "The chemical bond and the structure of molecules" was the absence of an historical approach to the development of the problem of the structure of chemical compounds. This led us to present a distorted picture of the real position of the given problem, and to an erroneous presentation of the principles on which are based modern conceptions of the structure of molecules. The theory of the structure of organic compounds, from which are derived present-day achievements of this branch of chemistry, stems from the work of Butlerov in the eighteen-sixties. Before then, as Butlerov said, organic chemistry was distinguished by the way in which experiment outdistanced theory. A great number of experimental facts had been accumulated, but there was no general idea, no general approach, which would allow of all this material being considered from a single viewpoint.

Many scientists, such as, for example, Kekule, held eclectic views, and did not appreciate the role of theory, not believing in the possibility of creating a unifying theory which could serve as a basis for the whole of organic chemistry. Kekule, Kolbe, and others believed that it was impossible to visualize the way in which mutual bonds between atoms in molecules exist. Agnosticism also typified the views of Gerard, who held that chemical methods may permit us to gain knowledge of the past or the future of molecules, but not of their present.

Under these conditions Butlerov's theory of chemical structure initiated an absolutely new period in the development of chemistry. It was from that time, i.e., after Butlerov had made his fundamental contributions, that the idea of chemical structure as the factor determining the chemical behavior of substances entered into chemistry. The exposition of modern theories of the structure of molecules must necessarily begin with an account of this period, as that of the beginnings of the science of chemical structure. Our very grave error was that we did not take into account the historical approach to the problem, that we treated its present state without reference to its historical development, and that we presented it as if our knowledge of the structure of molecules dated from the time when the quantum mechanics methods were applied to the estimation of the energy and of other properties of molecules.

In actual fact, the basis of modern views, and their origins, are those concepts of molecular structure which had been developed by Butlerov. An insufficient appreciation of the role of Butlerov and of his theory of chemical structure was the cause of the errors of our book. This theory, which lies at the basis of our modern concepts, was in effect thrown out of our book. Our mistake was that we reduced all the richness and the importance of the theory only to the dashes representing valency, and then wrote that the structural theory is a formal one.

In actual fact, Butlerov's theory of chemical structure contained profound ideas, which for long years determined the development of the whole of organic chemistry. The basic proposition of the theory of structure is the concept of the presence in each molecule of a definite order of atomic bonds, which are represented as structural formulas; it reflects the fact that a molecule is a qualitatively determined particle, possessing a unique and definite structure for each molecule. This is a profoundly materialistic idea, without which all the later development of the theory of structure would have been impossible. It is to Butlerov, who established the reality of the chemical structure of molecules that we owe the concept that the chemical behavior of substances is determined by their chemical structure.

Butlerov's formulation of the idea of chemical structure differs radically from the views of Kekule, or Cooper, who considered structural formulas to be only reaction formulas "transformation formulas". Thus the real author of the theory of structure is incontestably A. M. Butlerov.

All these circumstances were not presented in our book. We should also emphasize that the concept of chemical structure introduced by Butlerov is by no means confined only to the questions of location of atoms and distribution of bonds in a molecule.

One of the foundation stones of Butlerov's theory is the teaching about the mutual influence, the mutual action on each other of atoms, both directly combined and not combined.

According to Butlerov, chemical structure is the "distribution of the action of chemical forces (affinities), owing to which chemical atoms, by acting directly or indirectly on each other, combine to give chemical molecules".

In scientific matters Butlerov opposed, from a materialistic standpoint, scientific idealism which rejected the actual existence of atoms in molecules; he opposed creeping empiricism, which degraded the role of theory in science.

On the other hand, Butlerov's materialistic theory resulted from the acknowledgement of the reality of atoms and from a scientific conviction that it would be possible to study their properties. It is in this approach of Butlerov's that the materialistic tendency of Russian natural science was displayed. It is thanks to this that Butlerov's theory correctly depicts the basic features of the chemical form of the movement of matter.

Special mention should be made of the great significance of Butlerov's contribution to the question of the role of theory in scientific research. The predictive power of his theory stimulated a whole series of new discoveries. The impeccable theoretical argumentation and experimental confirmation characteristic of Butlerov's work are an illustration of unity of theory and practice. To this is ascribable the vitality of Butlerov's teaching on chemical structure.

We should note that Butlerov applied his theory of structure to the prediction of a number of compounds which were as yet unknown, and which he then synthesized, such as, for example, the tertiary alcohols. Butlerov also explained isomerism, and gave a correct theory of tautomerism. It should also be pointed out that Markovnikov, by making use of the concepts of reciprocal action on each other of atoms, was able to formulate his well-known rule for reactions of addition, substitution, and splitting off. This rule is a manifestation of the general laws of mutual influence of atoms and groups of atoms in molecules, and it is still today fully valid.

Butlerov's dynamic concept of the molecule was a brilliant anticipation of modern views of the nature of the molecule, as a complex dynamic system. It was this materialistic principle, characteristic of Russian science, which we should have emphasized, inasmuch as it was Butlerov's strength in his struggle against idealists and agnostics. One of the mistakes of our book, due to our disregard of general philosophical principles, was that we did not base our views on Butlerov's materialistic theory, from which alone could the study of the structure of molecules be developed. The absence of Butlerov's theory from our book was the reason why it became permeated with idealistic and mechanistic concepts. We should also have emphasized that our present-day views on the structure of atoms and molecules are based on M. V. Lomonosov's atomistic concept and on D. I. Mendeleev's periodic table. The over-estimation of second-rate work by foreign authors, and the under-estimation of the work of Soviet scientists were connected with the under-estimation of Butlerov's theory.

A serious shortcoming of our book is that it pays no attention to questions of methodology. In dealing with the theory of the chemical bond we did not take into account that this problem is directly concerned with the general philosophical and methodological problems of chemistry and physics. Actually, as is evidenced by a whole series of declarations made in the scientific press and at discussion meetings devoted to the theory of chemical structure, the very enunciation of the problem of the nature of the chemical bond involves the struggle between idealism and materialism. On the one hand we have the materialistic concept of the molecule as an objective reality, and on the other the pragmatic, agnostic approach, connected with the idealistic view of the unknowability of the molecule. In the latter case objective criteria of the reality of the molecule and of the chemical bond disappear. In our exposition of the problem of the nature of the chemical bond we did not consider methodological questions, and we did not criticize idealistic presentations.

Physical idealism and mathematical fetishism have largely infiltrated into chemistry in the form of the "resonance or mesomerism theory". The resonance theory derives from a formally incorrect interpretation of one of the approximative methods of quantum chemistry—the method of localized pairs. The sense of a definite chemical structure was ascribed to the individual terms of the sum approximately expressing the wave function describing the state of the molecule. In reality, the individual terms making up the wave function used as a first approximation possess only a purely mathematical significance, and are not connected with the real properties of objectively existing molecules. This incorrect interpretation led us to an erroneous concept of allegedly existing physical phenomena, viz., quantum-mechanical resonance structures, according to which superposition of resonance structures determines the real state of the molecule. We were in error in uncritically accepting this concept, and in applying it widely in our book, in which we frequently used such expressions as "is explained by resonance", "ascribable to presence of structures", or "ascribable to appearance of structures". Explanations based on the use of nonexistent structures must, of course, be erroneous, for since they are merely terms of a mathematical expression the individual terms of the development of a wave function cannot be the causes of physical effects. Such objectivization of a purely mathematical concept must be considered to be physical idealism. The resonance theory was an idealistic interpretation of the approximative method of localization of pairs. Other manifestations of this objectivization were such expressions as "structures co-exist in molecules" or "structures are represented", which might mislead one into thinking that real structures are intended. A mistaken belief in the existence of fictitious structures led us to a mistaken understanding of resonance as a phenomenon. The objective reality of a concrete form of motion of matter which determines the properties of actually existing states of molecules, independent of our consciousness of them, has been replaced in the resonance theory by purely speculative and subjective structures, having no real existence. Thereby objective reality was replaced by fictitious representations, and this is a manifestation of idealism in science.

We did not in our book subject the resonance theory to criticism from a philosophical angle, and we thus did not discern the Machist tendencies of its authors. Yet this should have been done, the more so as the authors of the "resonance theory" themselves treat resonance as a speculative concept, as a "convenient" descriptive method, for this reason accepted as correct; as we have seen, this is unconcealed Machism. The harm done to the natural sciences by concepts of this sort has been pointed out by V. I. Lenin in his work of genius "Materialism

and Empirio-criticism", in which he showed that the principle of economy, which is fundamental to the theory of cognition, must inevitably lead to subjective idealism. The multiplicity of structures inherent in the resonance theory is a deviation from the materialistic concept of Butlerov, and is a retrograde step towards the pre-Butlerov agnosticism of Gerard, Kekule, and others.

The resonance theory, being an erroneous interpretation of one of the approximative methods of calculation applied to multi-electronic systems, does not derive from quantum mechanics. The difficulty of approach to such complex systems lies in the fact that we do not know their real wave functions, describing the state of the system. For this reason, in the approximative methods known to us today, one of which is the method of electron pairs, or of valency schemes, the actual wave function is given approximately by certain mathematical expressions, which only very crudely reflect the nature of the actual wave function. It should here be pointed out that there may be various ways of approximating to a correct wave function. In quantum chemistry, in addition to linear combinations of derivatives of mono-electronic wave functions, used in the method of electron pairs, other mathematical approximations to the correct wave function are applied. Thus for a large number of problems the method of molecular orbits is used, based on a different approximation, which is in no way connected with "resonance structures". Other approaches are also possible, which do not necessarily make use of linear combinations of simpler functions. As an example of this, we would point out that in making calculations for the hydrogen molecule, which allowed of the calculation of the energy of formation of this molecule with a high degree of accuracy, use was made, as an approximative wave function, of an expression not based on a linear combination of mono-electronic functions. Thus we see that the use of linear combinations of derivatives of mono-electronic functions is only one of the particular and imperfect ways of arriving at an approximation to the correct wave function.

Resonance structures were made use of in the "resonance theory" as if they were ordinary structural formulas. Yet it should be realized that the individual terms of which the wave function is made up, in the method of electron pairs, are not connected with any experimentally observable physical data whatsoever. A physical sense is possessed only by the wave function itself, as a whole, being directly related to real physical characteristics of objectively existing molecules, such as the energy of molecules, the distribution within them of electric charges, etc.

Our mistake was that we did not give a clear-cut explanation, in the above sense, of the individual terms when dealing with wave functions, and that when we considered them separately from the particular mathematical operations to which they belonged we tended to regard them as if they were of the nature of primary factors, determining the actual physical properties of the molecule. This was an unjustifiable use of the individual components of a wave function; we raised them to the level of an absolute, independent of matter. The elevation of individual items of cognition to the rank of absolutes was, as we know, described by Lenin as being philosophical idealism: "from the view point of dialectical materialism philosophical idealism is a one-sided, exaggerated . . . hypertrophy (expansion, inflation) of one of the features, aspects, or facets of cognition into an absolute, detached from matter or from Nature, a deification".*

There is no trace of rationality in treating of individual terms of an analysis as objectively existing resonance structures. The posing of the imaginary problem of establishing experimentally the existence of separate "resonance structures" is a misunderstanding.

We, unfortunately, added to the methodological errors of the "resonance theory" by introducing the concept of transitional structures. On the grounds that the density of the electron cloud is expressed as the square of the wave function, and is thus represented in the form of the sum of the squares of the individual terms of the analysis and of their double derivatives, we connected the expression for the latter with separate "transitional structures". As a result, the individual terms of the sum, which are of purely mathematical origin, became objectivized, and were regarded as factors determining the properties of real molecules. In this case, too, a fictitious, imaginary picture was elevated to the status of a factor determining objectively real phenomena.

We did not in our book clearly differentiate between the concepts of state and structure, and this was one of the causes of our mistaken interpretation of individual components of the approximative wave function, insofar as we regarded these individual terms as separate states of the system, whereas in reality these terms of a mathematical expression do not relate to any states whatsoever which could exist in a molecule, i.e., they have no real physical sense.

It should be noted that a justified criticism of the "resonance theory" does not contradict the value of quantum-

* V. I. Lenin, *Philosophical Notes*, Gospolitizdat, 1947, p. 330.

chemical calculations based on existing methods. These calculations are very rough and imperfect ones. It is essentially a zero approximation, but it can in a number of cases be useful, as, for example, in comparing different molecules with conjugated bonds, or molecules with different kinds of annelation of benzene rings (acene, phenes), etc. The existing methods permit of the very approximate calculation of the total energy of π -bonds for the basal and the excited states. The final values derived for total energy are in no way connected with any reference to separate "resonance" structures. As for the quantum-mechanical method of molecular orbits, this has no connection at all with "separate structures", and it can find application in a limited range of problems (comparison of molecules with conjugated bonds). To this category belongs the calculation of transition from the singlet to the triplet, bi-radical state, etc.

The basic shortcoming of known quantum-chemical methods used in our work is their lack of precision. For this reason, where large effects of the order of tens or even hundreds of kg-calories are concerned, these methods, and particularly methods of molecular orbits, may be applied for comparative purposes. It should be borne in mind that because of their imprecision and approximative nature the applicability of these methods is very restricted. It should also be noted that although the application of quantum mechanics to chemistry may be of value for the provision of data relating to individual characteristic molecules, this approach cannot lead to the elucidation of the whole complex and specification of chemical phenomena. The further development of the theory of chemical structure should be based on synthesis of organic substances followed by a study of their reactivity and other chemical properties, in relation to their structure. Quantum-chemical methods can be of only auxiliary value in this study. Special caution must be exercised in applying the results obtained by quantum-chemical calculations for simple molecules to more complex ones; the result should always be checked by the data of chemical experimentation.

Inasmuch as the individual components of wave functions are not related to any experimentally observed real characteristics of molecules it is natural that the resonance structures considered cannot serve for the drawing of any conclusions relating to the objective properties of molecules. To this are due the mistakes made in the application of the "resonance theory" to chemistry. Explanations based on the use of resonance structures are only apparent ones, for, being a consequence of the incorrect interpretation of a method of calculation, the concept of resonance cannot give satisfactory explanations of chemical and physical facts. Our mistake was that we did not discern the nature of the "explanations" afforded by the "resonance theory", and that we made wide use of these "explanations". The application of resonance structures to the explanation of experimental facts opened up the way for arbitrary reasoning, inasmuch as the impression was created that explanations could be possible where in fact there was no explanation.

Resonance structures are used in the "resonance theory" for the explanation of experimental results. The first consequence of this is that the way is opened for finding "explanations" of experimental errors. Thus, for example, erroneous experimental data relating to the alleged increased distance between two methylene groups in dibenzyl were easily explained as being a consequence of the tendency of dibenzyl to break up into two tolyl radicals, owing to which the distance between the methylene groups is lengthened. Later experiments, however, showed that the distance in question is shortened, not lengthened. In the same way erroneous spectrometric data were explained by "proving" that the benzoyl ion causes an electron shift in the ring, and is an ortho-para orientator. This was readily accomplished by representing the structure of benzoic acid with a valency link between the two oxygens of the carboxyl group, as a result of which the negative charge was shifted to the ortho position of the ring. Later work showed, however, that the experimental data for which the explanation was given were erroneous. It was thus always possible to find any fictitious "structure" whatsoever, and to believe that nothing else needed to be done. The possibility then appeared of explaining complex, and at first sight inexplicable, facts by means of structures invented ad hoc to suit each case. For example, the shortened interatomic distances of organic fluorine derivatives were explained by ascribing to fluorine a bivalent state with a positive charge. Thus, specially for this given case, fluorine, that most electronegative of all the elements of Mendeleev's periodic table, becomes electropositive and bivalent. In this way apparent explanations were fabricated.

To the same category of errors belong explanations involving the reduction of chemical problems to structures or to the matching of structures with ordinary and stretched bonds. Formal schemes not conveying the real state of molecules are used in the "resonance theory" for writing structures. The possibility of improvising one or another structure thus arises, and not infrequently mutually exclusive assumptions are made from case to case. Thus, for example, for the explanation of the normal value of the moments of triphenyl-, fluoro-, chloro-, bromo-, and iodo-methane it is necessary to assume hindrance of the shift of negative charges from the benzene

rings to the electronegative halogens. But for the high dipole moment of nitrobenzene as compared with nitromethane it is assumed, on the contrary, that the shift of negative charges to the electronegative oxygen atoms of the nitro-group is facilitated. In this way the possibility of providing explanations for everything is furnished; such explanations cannot but be thought to be unsatisfactory.

The errors pointed out above, relating to the structure of molecules, also affected problems of reactivity as applied to molecules during reactions. According to how the reaction went this was said to be due to the molecules "reacting in one or another resonance form". This gave rise to erroneous views on the mechanism of a large number of organic reactions.

The procedure adopted, instead of making a critical examination of the reaction mechanism, was to write some resonance structure appropriate to the way the given reaction proceeded and to the nature of the end product, or arrows were appropriately distributed about the formula. It should be noted that our errors also apply to the mesomerism theory, to the same degree as to the "resonance theory". Every resonance structure may be represented by the aid of arrows.

Instead of establishing the real reaction mechanism (by means of kinetic measurements, by the method of labelled atoms, etc), the "theory of resonance or mesomerism" replaces the reaction process and its laws by selected structures or arrows, which are made to fit the results obtained by the use of unproven hypothetical ions, both positively and negatively charged, carbonium and carbanium ions, and a host of others which figure in the literature, and for whose existence there is often very little evidence. We did not, to our regret, expose these errors of the "resonance or mesomerism theory" as applied to reactivity, and the same mistakes acceptance of the theory is to be found in the work of a number of authors who gave theoretical explanations of experimental results in organic chemistry.

The "resonance or mesomerism theory" by giving baseless explanations of reaction mechanisms created an atmosphere of contentment with the apparently adequate theoretical basis provided for organic chemistry. Here, too, we were in error.

To summarize what we have said above, we have come to the conclusion that the "resonance or mesomerism theory" is one of the manifestations of idealism in science. It gives expression to bourgeois ideology in chemistry, in the same way as bourgeois ideology has infiltrated into other domains of science, on which creative discussion meetings have been held during recent years.

The sources of our mistakes were:

1. We were not sufficiently guided in our work by the principles of materialistic dialectics, which alone reflect the objective processes of the real world and its laws.
2. The absence of criticism and of verification of the scientific coherence of the theory of the chemical bond from the stand-point of dialectic materialism.
3. The under-estimation of the significance of the materialistic trend of the classical workers of Russian natural science, of their patriotism, and of their contributions to science.
4. An uncritical attitude towards the reactionary ideas of certain Western scientists, which are symptomatic of the decay of the moribund culture of capitalism.
5. An uncritical attitude towards the interpretation of the numerical results given by the approximative quantum-mechanical methods.

We shall in our future work make every effort towards the rectification of our mistakes. Our future task will be to contribute to the development of knowledge of the structure of molecules on the lines of the teachings of dialectical materialism and of the ideas of Butlerov, Mendeleev, Markovnikov, and other coryphes of Russian science.

It is necessary to make the widest possible use of the scientific heritage of Butlerov, and, basing ourselves on his first propositions in the domain of the theory of chemical structure, to generalize the material since accumulated so as further to develop the theory of chemical structure with the help of the achievements of quantum mechanics.

The essential problem to which attention should be directed is that of the connection between chemical structure of molecules and their reactivity. This work should be conducted by means of studies of the kinetics of the reaction, and by the use of labelled atoms, with the object of elucidating reaction mechanism, estimating the strength of bonds, their equivalence or non-equivalence, elucidating the question of the part played by

radicals, ions, and other intermediate products in chemical reactions, and of investigating the role of the solvent in chemical processes. The elucidation of the role of thermodynamic and kinetic factors in determining the course of chemical reactions is also of importance.

A second approach to be used in our work in this domain should be the further experimental study of the physical properties of molecules, and in particular of their polarity, by measurements of dipole moments, of the magnetic properties of chemical compounds, with the object of elucidating the valency state of the atoms, and the types of bonds between them, and of their optical properties. The object of work in this direction should be to obtain data on the structure of molecules and to elucidate the nature of the reciprocal effects between atoms and groups in molecules.

One of the tasks before us is the application of the methods of quantum chemistry to the solution of particular problems connected with the mutual effects on each other of atoms in molecules, as an approach to the problem of the interaction of σ - and π -bonds and to the question of directional valencies and valency states of atoms. At the same time we believe that the existing methods of quantum chemistry can, in view of their very approximative nature, have only a very limited sphere of applicability, and need to be perfected.

It is necessary, in the domains of reactivity, structure, and the study of the physical properties of molecules, to explore those problems which would be of help in solving the practical problems which confront chemical industry.

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FREE ENERGY AND HEAT OF DEHYDRATION OF CRYSTAL-HYDRATES OF URANYL NITRATE AND CHLORIDE

A. F. Kapustinsky and L. I. Baranova

There are no published data relating to the free energy of dehydration of crystal hydrates of uranyl salts, and only a very few measurements have been made of heats of hydration of a few uranyl salts, by the calorimetric method [1]. We shall in this paper present the results of tensimetric determinations of the dissociation pressure of uranyl nitrate hexahydrate and uranyl chloride trihydrate at various temperatures, from which the free energy and the thermal effects of the reaction may be derived.

A tensimeter of the Frowein type was used, in which the number of ground joints was reduced, but their dimensions were increased, and mercury seals were introduced. The experimental and the standard substances were placed in bulbs *a* and *b* of the tensimeter (Fig. 1), and the bulbs were connected by the joints *d* and *e*, fitted with mercury seals, to a differential mercury manometer, on one limb of which was a bulb *c* which served as a reservoir for the mercury when the manometer was held in a horizontal position during evacuation. A large vacuum tap *k* separated the instrument from a steam trap and an oil pump giving a vacuum of 0.01 mm. Vacuum grease was used for the taps and joints, and redistilled mercury was taken for the manometer.

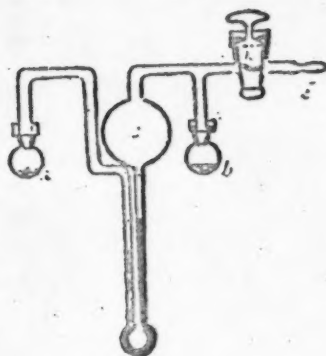


Fig. 1. Diagram of tensimeter.

The instrument did not leak for several days at 55°. The temperatures used were $25^\circ \pm 0.005^\circ$ and $50^\circ \pm 0.05^\circ$. The constancy of temperature was checked with the aid of a Beckman thermometer, and temperatures were read on a normal thermometer graduated in 0.1°, calibrated at VIMS. Pressure was read with the aid of a microscope-vernier with a nonius checked against a standard, the accuracy of reading being 0.1-0.05 mm. The reference substances taken were water and sulfuric acid of a concentration giving a water vapor pressure of 0.008 mm. The ordinary conditions necessary for tensimetry were observed. The results were checked by measurements of the dissociation pressure of crystal hydrates of copper sulfate, which can readily be obtained pure, and which have been extensively studied.

We approached each equilibrium from both sides (with rising and with falling temperature). The time taken for establishment of equilibrium was different for different crystal hydrates, being

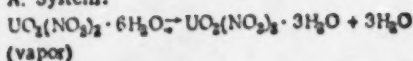
of the order of minutes for hexahydrate, 60-70 hr for the trihydrate of uranyl nitrate, and 30-40 hr for the trihydrate of uranyl chloride. Well reproducible results were obtained for all the salts. Each value recorded for the dissociation pressures is the mean of a least two measurements differing by not more than 1%. The salts were prepared from chemically pure specimens from the Mendeleev Institute collection. Uranyl nitrate hexahydrate was recrystallized four times, after which it was analyzed by precipitation with ammonia according to Hillebrand, and was found to contain 5.8 molecules of water. The powdered crystals were kept in a vacuum desiccator over 35% sulfuric acid, to constant weight. The trihydrate was prepared by keeping the hexahydrate over 65% sulfuric acid for 4 weeks, constant weight being achieved after the loss of 2.94 mol of water. The trihydrate of uranyl chloride was prepared similarly. Lewenstein [2] has confirmed earlier work showing the existence of these hydrates, giving the intervals of concentration of sulfuric acid corresponding with the equilibrium points of the appropriate crystal hydrates.

It is known [3] that as a result of the hydrolysis of uranyl chloride by its own water of crystallization at temperatures above 90° hydrogen chloride is evolved. We performed special experiments with the object of finding

* All-Union Institute of Mineral Raw Materials.

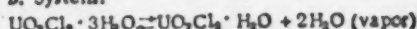
TABLE 1

A. System:



Temperature, °C	25	30	35	40
Vapor pressure of water vapor, mm	7.1	10.3	14.8	21.3

B. System:



Temperature, °C	35	40	45	50
Vapor pressure of water vapor, mm	2.1	3.1	4.8	6.7

out whether this hydrolytic reaction takes place at the highest temperatures used by us, viz., 50°; dry air was passed at a rate of 10 liter/hr through uranyl chloride hydrate, and then through silver nitrate solution, for several hours. The solution became opalescent, although no precipitate was formed. This result corresponds with a dissociation pressure (with evolution of hydrogen chloride) of the order of 10^{-7} mm, i.e., hydrolytic decomposition of the salt is practically absent at temperatures below 50°. The specimen of uranyl chloride trihydrate was twice recrystallized, and was then kept in a vacuum desiccator over 65% sulfuric acid; its purity was checked by analyzing it by Hecht and Danz's hydroxyquinoline method. The results obtained are presented in Table 1.

The results are in good agreement with a linear relationship between $\log p$ and $1/T$. The curves of Figs. 2

and 3 are constructed by the method of least squares, for the systems A and B. The equations of the curves are

$$(A) \quad \log p = -\frac{2949}{T} + 10.74 \quad (1)$$

$$(B) \quad \log p = -\frac{3157}{T} + 10.58 \quad (2)$$

and from them may be derived the standard heats and free energies of hydration. For system (A) $\Delta H = -13.49$ kcal and $\Delta F = -8.3$ kcal, while for system (B) $\Delta H = -14.44$ kcal and $\Delta F = -7.2$ kcal (at 35°).

As for the system uranyl nitrate trihydrate-dihydrate and water, the results obtained were much less reproducible. The relevant equation:

$$\log p = -\frac{2896}{T} + 9.87 \quad (3)$$

gives $\Delta H_{298} = -13.3$ kcal. This value, as well as that for free energy (-0.8), must, however, be regarded as no more than a rough approximation, for which reason they are inserted in parentheses in Table 2.

Our values are in good agreement with published figures; derived from calorimetric measurements of heats of dissolution. Thus for system (A) $\Delta H_{298} = -13.0$ kcal according to de Forcrand [4], -12.92 kcal according to Katzin, Simon, and Ferraro [5], and -13.49 kcal according to us, and for the system trihydrate-dihydrate and water, for the same salt, the thermal effect is -13.8 kcal according to de Forcrand, -14.2 kcal according to Katzin, Simon and Ferraro, and -13.3 kcal according to us. We have been unable to trace any published studies on uranyl chloride.

TABLE 2

Reaction	Heat and free energy, kcal	
	ΔH_{298}	ΔF_{298}
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{O}$	-13.49	-8.3
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}$	(-13.3)	(-0.8)
$\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O}$	-14.44	-7.2
	(at 35°)	

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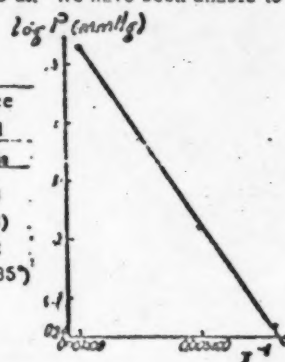


Fig. 2. Relation between the logarithm of the dissociation pressure of uranyl nitrate hexahydrate and $1/T$.

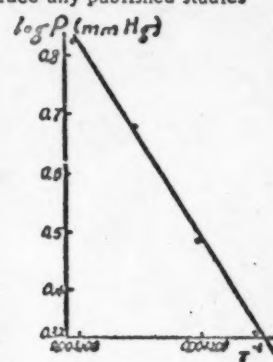


Fig. 3. Relation between the logarithm of the dissociation pressure of uranyl nitrate hexahydrate and $1/T$.

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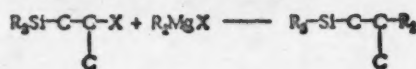
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SYNTHESIS OF SILICOHYDROCARBONS FROM β -SILICOHALIDES AND ALKYL-LITHIUM *

A. D. Petrov and V. P. Lavrishchev

Petrov and Mironov [1] have shown that in the syntheses of silicohydrocarbons by the condensation of secondary β -silicohalides with Grignard reagents:



where R_1 is Et or Pr, the yields rise with increase in the length of the radicals R from Me to Bu.

TABLE 1

Condensation product	Yield as % of	
	$R_3Si-C\equiv C$ taken	R_3Li
$ \begin{array}{c} Me_3Si-C-C-C-C-C \\ \\ C \end{array} $	0.6	21.8
$ \begin{array}{c} Et_3Si-C-C-C-C-C \\ \\ C \end{array} $	9	27
$ \begin{array}{c} Et_3Si-C-C-C-C-C \\ \quad \\ C \quad C \end{array} $	3.6	26
$ \begin{array}{c} \quad \quad C \\ \quad \quad \\ Et_3Si-C-C-C-C \\ \quad \\ C \quad C \end{array} $	0	6.1
$ \begin{array}{c} \quad \quad C \\ \quad \quad \\ Et_3Si-C-C-C-C \\ \quad \diagdown \quad \diagup \\ C \quad \quad C \quad C \end{array} $	17.4	-
$ \begin{array}{c} Bu_3Si-C-C-C-C-C \\ \\ C \end{array} $	4	20
$ \begin{array}{c} Bu_3Si-C-C-C-C-C \\ \\ C \end{array} $	-	18

Compounds of the type R_3SiR_4 , which are the chief product of β -decomposition, were not found, showing that if this takes place at all it must be to a smaller extent than with R_1MgX . The main products were obtained in yields of 20-27%, and the by-products in yields of 8-12%. Where low yields of product were obtained, such as 6% with *tert.* butyl lithium, the yield of by-products rose to 33%.

It is of interest that in the condensation of triethyl- β -bromopropylsilane with $\text{Cl-Mg}-\text{C}(\text{CH}_3)_2-\text{CH}_3$, where tert. butyl did not enter into the reaction of condensation, and where triethyl-tert-butylsilane could also not be obtained, the reduction product, triethylpropylsilane, was obtained in 11% yield, and the product of condensation of the silyl halide, 1,4-di-(triethylsilyl)-2,3-dimethylbutane, in 6% yield.

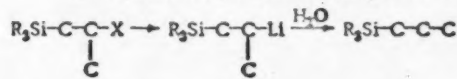
We undertook the study of the condensation of secondary β -silico-halides with Grignard reagents containing radicals R_1 likely to give rise to steric hindrance, such as $n\text{-C}_4\text{H}_9$, $\text{iso-C}_4\text{H}_9$, $\text{iso-C}_3\text{H}_7$, and $\text{tert. C}_4\text{H}_9$.

Our experiments showed that much lower yields are obtained with these reagents, falling to zero for tert. C_4H_9 . There are numerous indications in the literature that in the synthesis of silicohydrocarbons from silicohalides with the halogen attached to the silicon atom much higher yields are obtained when alkyl-lithium is used instead of Grignard reagent [2].

It was thought to be of interest to find out whether a similar effect is obtained when β -silicohalides are taken. As appears from Table 1 this was found to be the case. Not only does the substitution of lithium for Grignard reagents raise the yields by as much as 3-6 times, but it also allows of the introduction of such sterically difficult radicals as is tertiary butyl. The use of alkyl-lithium instead of Grignard reagents also affects the nature of the by-products of the reaction.

The side reactions taking place with alkyl-lithiums are:

1. Reduction of β -silane halides, as follows:



2. Condensation, as follows:

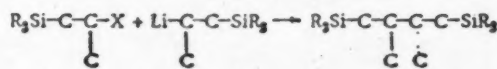


TABLE 2

$(C_4H_9)_3Si-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_2-CH_2-CH_2-CH_3$ B.p. 236-238°; d_4^{20} 0.7959; n_D^{20} 1.4448	Found %: C 72.72; 72.52; H 13.62; 13.48; Si 12.81; 13.55 $C_{13}H_{28}Si$ Calculated %: C 72.8; H 14.1; Si 13.1
$(C_4H_9)_3Si-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_3$ B.p. 233-234°; d_4^{20} 0.7979; n_D^{20} 1.4454	
$(C_4H_9)_3Si-CH_2-\underset{\substack{ \\ CH_3}}{CH}-\underset{\substack{ \\ CH_3}}{C}-CH_3$ B.p. 229-230°; d_4^{20} 0.8050; n_D^{20} 1.4492	
$(C_4H_9)_3Si-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH-\underset{\substack{ \\ CH_3}}{CH_3}$ B.p. 221-222°; d_4^{20} 0.7993; n_D^{20} 1.4460	Found %: C 72.5; 72.54; H 14.2; 13.92; Si 13.5; 13.62 $C_{12}H_{24}Si$ Calculated %: C 72.0; H 14.0; Si 14.0
$(n-C_4H_9)_3Si-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_2-CH_2-CH_2-CH_3$ B.p. 306-306.5°; d_4^{20} 0.8054; n_D^{20} 1.4512	Found %: Si 10.67; 10.59 $C_{15}H_{32}Si$ Calculated %: Si 9.42
$(CH_3)_3Si-\underset{\substack{ \\ CH_3}}{CH}-CH_2-CH_2-CH_2-CH_3$ B.p. 175-176°; d_4^{20} 0.7517; n_D^{20} 1.4222	
$(n-C_4H_9)_3Si-CH_2-CH_2-CH_3$ B.p. 267-268°; d_4^{20} 0.7949; n_D^{20} 1.4462	
$(C_4H_9)_3Si-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH-\underset{\substack{ \\ CH_3}}{CH_2}-Si(C_4H_9)_3$ B.p. 314-317°; d_4^{20} 0.8376; n_D^{20} 1.4672	
$(n-C_4H_9)_3Si-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_2-CH_2-CH_3$ B.p. 290-290.2°; d_4^{20} 0.8038; n_D^{20} 1.4500	

EXPERIMENTAL

The conditions used in typical alkyl-lithium syntheses are as follows. 51.2 g of β -bromopropyltrimethylsilane was added during 15 min. to 40 g of BuLi, with vigorous stirring; considerable evolution of heat was observed. The mixture was treated with ice and 10% HCl, the ether layer was separated and dried. Distillation gave 9.8 g of β -butylpropyltrimethylsilane (yield 21.8%) and 2 g of 1,4-di-(trimethylsilyl)-2,3-dimethylbutane (yield 5%). Under similar conditions 42.75 g of β -bromopropyltributylsilane and 30 g of BuLi gave 8 g of $Bu_3Si-CH_2-\underset{\substack{| \\ CH_3}}{CH}-CH_2-CH_2-CH_2-CH_3$ (yield 20%) and 2 g of $Bu_3Si-CH_2-CH_2-CH_3$. In addition, a small amount

of high b.p. products was obtained, but no individual silanes were isolated. The properties of the asymmetrical monosilanes of the C_{12} - C_{15} series obtained are given in Table 2, as well as those of one of the disilanes.

We also attempted the condensation of β -bromopropyltriethylsilane with EtLi, and in this case too the yield of condensation products was about the same as with higher molecular weight radicals, viz., 23.4%, and reduction and condensation products were also found among the by-products.

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* See Consultants Bureau English Translation, p. 591.

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SYNTHESIS AND PROPERTIES OF UNSATURATED SILICOHYDROCARBONS: DIMETHYLDI-(METHYLALLYL)SILANE, METHYLDI-(METHYLALLYL)SILANE, METHYLTRI-(METHYLALLYL)SILANE, TETRA-(METHYLALLYL)-SILANE, TRIMETHYLCYCLOPENTADIENYLSILANE, AND TRIMETHYLBUT-3-ENYLSILANE

A. D. Petrov and G. I. Nikishin

Whereas there are numerous references in the literature to the synthesis and properties of mono-, di-, tri-, and tetra-allylsilanes [1], it is only recently that Petrov and Mironov [2] reported the synthesis of the first representative of the homologous methylallyl series—triethylmethylallylsilane. Continuing these studies, we prepared silicohydrocarbons with two, three, and four methylallyl radicals. The yields of these silicohydrocarbons, prepared by Grignard synthesis from the appropriate silyl halides and isobutenyl halide by the Yavorsky procedure, ranged from 35 to 45%, and were thus somewhat lower than those of allylsilanes. It was also noticed that these yields were, in the cases of tri- and tetra-methylallylsilanes, obtained only by vacuum fractionation of the reaction products; the yields obtained from distillation at atmospheric pressure were much lower, because of partial thermopolymerization of the methylallylsilanes, giving high b.p. products. It might be concluded that methylallylsilanes enter into polymerization and copolymerization reactions more readily than do allylsilanes.

Trimethylcyclopentadienylsilane and trimethylbut-3-enylsilane were synthesized, for the purpose of making a comparative study of the ease of polymerization of different silicohydrocarbons. The second of these silicohydrocarbons is of additional interest in that it is the first known compound of this class with a double bond in the γ -position. As is known from the literature [3] vinylsilanes are difficultly polymerizable, owing to the effect exerted by the silicon atom, whereas polymerization of allylsilanes proceeds very readily.

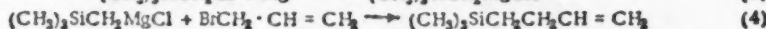
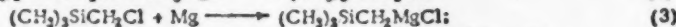
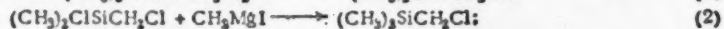
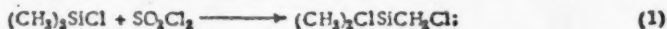
Trimethylcyclopentadienylsilane was prepared as follows. Butyl-lithium and cyclopentadiene gave cyclopentadienyl-lithium:



This, with trimethylchlorosilane, gave what appeared to be a mixture of 1- and 2-trimethylcyclopentadienylsilane, as appears from the change in its properties when it is redistilled:



Trimethylcyclopentadienylsilane (or 1-trimethylsilylcyclopentadiene) was condensed by a Diels-Alder reaction with maleic anhydride, giving an adduct of m.p. 102°. Trimethylbut-3-enylsilane was obtained by the following reactions:

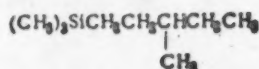


Chlorination of trimethylchlorosilane with sulfuryl chloride [4] gave dimethylchloromethylchlorosilane (35% yield), which with CH_3MgI afforded trimethylchloromethylsilane (60% yield), and this gave a Grignard reagent [5], which with allyl bromide yielded $(\text{CH}_3)_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (65% yield). Since we possessed this product, with the double bond in the γ -position, we thought it would be of interest to ascertain how hydrogen bromide adds on to the double bond.

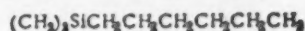
There are numerous indications in the literature of the nonequivalence of carbon atoms at different distances from the silicon atom, and of alternation of charges along the chain: $\text{Si}-\overset{+}{\text{C}}-\overset{-}{\text{C}}-\overset{+}{\text{C}}-\overset{-}{\text{C}}$. The physicist Fajans [6] considered that such an alternation was indicated by his refractometric studies. Accepting, however, alternation of charges along the chain, we still know nothing of how the magnitude and the distribution of these charges change under the influence of the reacting substances. We know that HBr adds on to trialkylvinyl-

silane in the opposite way to the Markovnikov rule [2,7], but to trialkylallylsilane according to this rule [8]. HBr also adds on to the double bond in the δ -position according to Markovnikov's rule, as was shown recently [9] for $(\text{CH}_3)_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$.

As a result of addition of HBr to the double bond in the γ -position, and of condensation of the bromide with MgBrC_2H_5 the silicohydrocarbon (I) was obtained:



This was shown by the synthesis of the isomeric hydrocarbon (II):



and by the establishment of their different physical properties and Raman spectra. This result shows that alternation of charges causing reversal of the order of addition of HBr to the double bond ceases at the β -position.

EXPERIMENTAL

Synthesis of methylallylsilanes. Isobutenyl chloride was prepared by the method of Kazansky and Lukina [10], about a kg. being obtained.

TABLE

Properties of methylallylsilanes

CH_3	Found %: C 70.01; 70.26; H 11.71; 11.81; Si 16.06; 16.23;	Yield in %
$(\text{CH}_3)_3\text{Si}(\text{CH}_2-\text{C}=\text{CH}_2)_3$	$\text{C}_{10}\text{H}_{18}\text{Si}$. Calculated %: C 71.35; H 11.91; Si 16.67	48
b.p. 178-178.5°; n_D^{20} 1.4515; d_4^{20} 0.8012		
CH_3	Found %: C 68.68; 69.02; H 11.82; 11.67; Si 17.71; 17.94	
$(\text{CH}_3)_2\text{HSi}(\text{CH}_2-\text{C}=\text{CH}_2)_3$	$\text{C}_9\text{H}_{16}\text{Si}$. Calculated %: C 70.05; H 11.75; Si 18.18	21.3
b.p. 61-63° at 17 mm; n_D^{20} 1.4550; d_4^{20} 0.7885		
CH_3	Found %: C 75.24; 75.00; H 11.78; 11.67; Si 12.43; 12.40	
$(\text{CH}_3)_2\text{Si}(\text{CH}_2-\text{C}=\text{CH}_2)_3$	$\text{C}_{12}\text{H}_{24}\text{Si}$. Calculated %: C 75.00; H 11.54; Si 13.48	35
b.p. 231.9-232.1°; n_D^{20} 1.4772; d_4^{20} 0.8338		
$\text{Si}(\text{CH}_2-\text{C}=\text{CH}_2)_4$	Found %: C 76.22; 76.55; H 11.05; 11.20; Si 11.68; 10.95	
CH_3	$\text{C}_{12}\text{H}_{24}\text{Si}$. Calculated %: C 77.4; H 11.3; Si 11.3	40
b.p. 269.5-270.5°; (130-133 at 11 mm); n_D^{20} 1.4950; d_4^{20} 0.8609		

The synthesis of dimethyldi-(methylallyl)silane and methyldi-(methylallyl)-silane was effected by boiling the substrates in ethereal solution for 20 hrs. Higher temperatures were required for the syntheses of methyltri-(methylallyl)silane and tetra-(methylallyl)silane. After boiling the ethereal solution for 2 hrs the ether was distilled off, xylene was added, and the solutions were boiled on an oil-bath for 12 hrs. The synthesis of the corresponding allylsilanes did not require such drastic conditions (distilling off the ether, and raising the temperature to 130°) [1,2]. The properties of the methylallylsilanes, and the yields obtained are given in the Table.

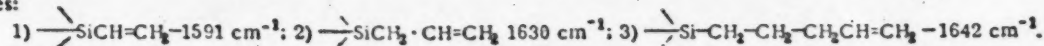
Synthesis of trimethylcyclopentadienylsilane. Butyl-lithium was prepared from 7.9 g of lithium and 82.2 g of butyl bromide, and 34 g of freshly distilled cyclopentadiene is added dropwise during 40 min. to the ethereal

solution, cooling the flask with ice-water, and passing a stream of nitrogen to exclude air. 65 g of trimethylchlorosilane was then added, and the mixture was left overnight, and boiled the next day for 12 hr under reflux. The solution was then filtered off from the white precipitate which forms, and water was added to the filtrate. The product was fractionated, giving 9 g of product, b.p. 138-140°, n_D^{20} 1.4622, d_4^{20} 0.8308. 2.1 g of maleic anhydride was added to a solution of 3 g of this product in 10 ml of ether; the reaction proceeded vigorously, all of the maleic anhydride going into solution within 5 min. After an hour a voluminous precipitate of transparent colorless crystals had formed; the product melted at 102-102.5° after two recrystallizations from ether.

Synthesis of trimethylbut-3-enylsilane. We shall here describe only the final stages of the reaction, which have not previously been reported in the literature. The Grignard reagent prepared from 8.2 g of magnesium and 41 g of trimethylchloromethylsilane was added to a solution of 50 g of allyl bromide in 50 ml of ether. Heat was evolved, and the solution boiled for a short time. The solution was left overnight, and then boiled under reflux for 12 hrs, after which the ether was distilled off, and the residue was heated on a water-bath at 70-80° for 8 hrs.

Fractional distillation gave 27.4 g of trimethylbut-3-enylsilane, b.p. 111.5-112.5°, n_D^{20} 1.4148, d_4^{20} 0.7358, MR_D found 43.66, calculated 43.70. The Raman spectrum was*: 148(2), 207(5), 247(2), 271(1), 324(3), 521(3), 577(3), 588(9), 616(4), 637(3), 692(6), 899(1), 940(3), 1014(2), 1103(3), 1173(3), 1280(7), 1298(6), 1415(8), 1639(10), 2845(5), 2897(20), 2959(8), 3002(6), 3080(5).

The characteristic frequency of the double bond in the γ -position, 1639 cm^{-1} , fits satisfactorily into the series:



Saturation of the silicohydrocarbon with HBr gave a bromide, b.p. 64° at 15 mm; n_D^{20} 1.4542; d_4^{20} 1.0894; found MR_D 52.02; calculated MR_D 51.85.

This bromide was added to magnesium ethyl bromide in ether. There was no visible evidence of any reaction, but after distilling off the ether a precipitate formed, with evolution of heat. The product was heated at 100° for 10 hrs, and water was then added. The product was distilled, giving a 22% yield of a product which we identified as trimethyl-3-methylpentylsilane (silicohydrocarbon D), b.p. 154-154.3°, n_D^{20} 1.4170; d_4^{20} 0.7450; found MR_D 53.44; calculated MR_D 53.43. The physical constants of this silicohydrocarbon and its Raman spectrum differ markedly from those of trimethyl-n-hexylsilane (silicohydrocarbon II) b.p. 160-162°, n_D^{20} 1.4153, d_4^{20} 0.7422).

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* I am indebted to Yu. P. Egorov for the Raman spectra.

** See Consultants Bureau English Translation, p. 537.

*** Evidently a typographical error remains uncorrected in this reference. No report by Yakovlev appears in the Journal of General Chemistry USSR, Vol. XIX, 1949, Publisher.

**** See Consultants Bureau English Translation, p. 591.

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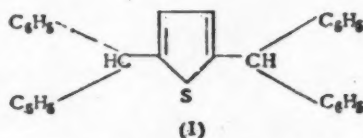
STRUCTURE AND CERTAIN PROPERTIES OF DIBENZHYDRYLTHIOPHEN

Ya. L. Goldfarb and M. S. Kondakova

We know that the reason for the common properties of systems of the type benzene, thiophen, furan, pyrrole, and others has been considered [1] to be their possession of an electron sextet, the so-called aromatic sextet. This schematic representation, which is essentially an electronic interpretation of Bamberger's early views [2], does not take into account a whole series of features of heterocyclic compounds, such as the retention by the salts of some alkylpyrroles of aromatic properties [3], or furan reacting as a diene. It is nevertheless of interest to obtain new experimental data relating to the role of the electron sextet as a carrier of aromatic properties. In this connection a comparison of the properties of thiophen, as an aromatic system, with those of its corresponding sulfone would be instructive; in the latter compound one should expect, on purely formal grounds, that parallel with the loss of aromatic properties the appearance of diene-properties would be observed.

Thiophen itself does not form a sulfone; di- and tetra-oxythiophen, described by Lanfry [4], are not sulfones, according to Hinsberg [5] (see also [6] and [7]). To the best of our knowledge there have been no papers published describing the sulfones of alkyl and aralkyl thiophens. This type of sulfone should, however, represent the most suitable material for the present research.

With this object we undertook the synthesis of the sulfone of dibenzhydrylthiophen. Dibenzhydrylthiophen is readily prepared from a mixture of thiophen and benzhydrol or benzhydryl ethyl ether by the action of stannous chloride [8]. From the nature of its formation it follows that substitution must have taken place in positions 2 and 5. This is confirmed by the results of hydrogenolysis, using a Raney nickel catalyst (see experimental section). The hydrocarbon so obtained has the composition and m.p. (122-123°) of 1,1,6,6-tetraphenylhexane ($C_6H_5)_2CH(CH_2)_4CH(C_6H_5)_2$, described by Vorlander et al. [9]; its solubility in ethanol differs from that given by these authors. For this reason we repeated Vorlander's synthesis, using N. M. Kizhner's instead of Klemmensen's method in the reduction of 1,1,6,6-tetraphenylhexa-3,4-dione. Contrary to Vorlander's observation, the hydrocarbon so obtained is relatively sparingly soluble in hot ethanol; its mixed m.p. with the hydrocarbon obtained from dibenzhydrylthiophen shows no depression. The structure of this product may therefore be taken as corresponding with that of 1,1,6,6-tetraphenylhexane, and our dibenzhydrylthiophen must be substituted in the 2,5-position:



Compound (I) gave the corresponding sulfone when treated with perhydrol, under the conditions described below. This product, like the great majority of sulfones, is not reduced by zinc in hydrochloric and acetic acid, but it is partly converted into 1,1,6,6-tetraphenylhexane by the action of spongy nickel catalyst. It does not give an addition product with excess of maleic anhydride at 200-220° or in boiling nitrobenzene, and it is not acetylated under the conditions for formation of the corresponding ketone from dibenzhydrylthiophen [8]. It reacts very slowly at room temperature with bromine in chloroform solution, without any perceptible evolution of hydrogen bromide; the product contains two atoms of bromine, apparently in the 1,4-positions. Under similar conditions dibenzhydrylthiophen gives a mono-bromo-derivative; since its oxidation products include benzophenone it follows that the bromine atom must be in the thiophen ring.

Thus the addition of two atoms of oxygen to the sulfur atom of dibenzhydrylthiophen involves loss of the tendency of atoms 3 and 4 of the thiophen ring to be substituted by halogen or acetyl, i.e., loss of aromatic properties. At the same time the sulfone does not react as a diene with maleic anhydride.

We do not yet know, however, whether this lack of reactivity with maleic anhydride is a feature of all sulfones of alkyl and aralkyl thiophens, or whether it is due to steric hindrance in the given case only.

EXPERIMENTAL*

1. Hydrogenolysis of dibenzhydrylthiophen. 25 g of spongy nickel catalyst is added to a solution of 5 g of dibenzhydrylthiophen in 100 ml of dry toluene (the catalyst was prepared by Mosingo's method [10]). The mixture was heated to boiling during 4 hrs, and then left overnight. The nickel was then filtered off and washed with several portions of toluene. The toluene was distilled off from the filtrate + washings, leaving about 5 g of crystalline product, m.p. 110-116°, recrystallization of which from ethanol gave two lots of crystals: 1.5 g of m.p. 83-107°, and 2.4 g of m.p. 121-123°, rising to 122-123° after a second recrystallization from ethanol, in which it is sparingly soluble in the hot.

Found %: C 92.18; 92.46; H 7.61; 7.76
 $C_{30}H_{20}$ Calculated %: C 92.30; H 7.7

The product gave no depression of m.p. when mixed with 1,1,6,6-tetraphenylhexane (see below).

2. Preparation of 1,1,6,6-tetraphenylhexane. A mixture of 0.5 g of 1,1,6,6-tetraphenylhexa-3,4-dione (m.p. 188-189°; prepared by Vorlander's method), 0.2 g of sodium in 7.25 ml of absolute alcohol, and 1.5 g of hydrazine hydrate solution (56%) was heated at 190-200° for 29 hrs in a small autoclave, and the solid product was separated and mixed with a small amount of water. The mixture was repeatedly extracted with ether, the extract was washed with water, and the ether was distilled off, leaving 0.2 g of residue, m.p. 118-120°, sparingly soluble in hot alcohol. Recrystallization from alcohol gave 1,1,6,6-tetraphenylhexane, m.p. 123-124.5°.

3. Action of perhydrol on 2,5-dibenzhydrylthiophen. 8 g of 28% perhydrol was added at room temperature to 4.16 g of dibenzhydrylthiophen in 25 ml of glacial acetic acid. The precipitate which forms gradually redissolves as the mixture is heated. The temperature was maintained at 104-105° for 25 min., and the solution on cooling deposited 4.5 g of crystalline product, m.p. 158-163°, which after recrystallization from alcohol gave 2.2 g of a product of m.p. 171-173°, raised to 172-173° by further recrystallization.

Found %: C 80.65; 80.60; H 5.50; 5.56; S 7.06; 6.92
 $C_{30}H_{24}O_2S$ Calculated %: C 80.35; H 5.35; S 7.14

2,5-Dibenzhydrylthiophen-1,1-oxide is insoluble in alkalis. It is readily soluble in chloroform, benzene, and toluene, soluble in hot alcohol and in hot acetic acid, and sparingly soluble in hot heptane. It is not reduced by zinc with a boiling mixture of hydrochloric and acetic acid.

4. Bromination of 2,5-dibenzhydrylthiophen. A solution of 1.1 g of bromine (0.0068 mol) in 20 ml of chloroform was added gradually to 1.5 g (0.0036 mol) of dibenzhydrylthiophen in 15 ml of chloroform, and the mixture was left at room temperature for 4 hrs, after which the chloroform was distilled off, leaving a resinous residue, part of which was soluble in hot alcohol. A yellow precipitate separated from the alcoholic solution on cooling. This was collected, giving 0.4 g of product, m.p. 125-126°, raised to 127-129° by further recrystallization from alcohol; pale yellow needles.

Found %: C 72.51; 72.25; H 4.79; 4.55; S 6.07; 6.16; Br 16.52; 16.33
 $C_{30}H_{22}BrS$ Calculated %: C 72.72; H 4.64; S 6.46; Br 16.16

5. Oxidation of the bromo-derivative of dibenzhydrylthiophen. A mixture of 1.3 g of bromodibenzhydrylthiophen, 3 g of CrO_3 , and 65 ml of acetic acid was heated on a water-bath for 4 hrs, the mixture was poured into water, and extracted with ether. The extract was washed successively with 5% aqueous sodium carbonate, 5% aqueous KOH, and water, and dried with $MgSO_4$. The ether was distilled off, leaving 0.75 g of an oil, which crystallized when seeded with a crystal of benzophenone. The redistilled product melted at 42-44°, mixed m.p. with benzophenone 44-46°.

6. Reduction of 2,5-dibenzhydrylthiophen-1,1-dioxide. A solution of 1.2 g of the dioxide in 10 ml of toluene was added to a flask containing 40 ml of dry toluene and nickel catalyst prepared by Mosingo's method [10], and the mixture was boiled, with stirring, for 7 hrs., after which it was filtered, and toluene was distilled off from the filtrate. The residue crystallized after addition of a small amount of heptane. The product was extracted with hot benzene-heptane mixture, and the solution was filtered off from insoluble residue. After standing, the filtrate deposits three crops of crystals. The first consisted of unchanged dioxide, and the other two (0.25 g), m.p. 117-125°, of a hydrocarbon, which after recrystallization from alcohol, melted at 122-123°, not depressing the m.p. of 1,1,6,6-tetraphenylhexane.

* With Z. V. Volodina.

oxide. A solution of 0.5 g of bromine in 3 ml of
dibenzhydrylthiophen-1,1-dioxide in 6 ml of chloroform,
during which time evolution of hydrogen bromide was
observed, leaving a pasty brown mass, which was
then recrystallized from benzene-heptane mixture,
in alcohol and heptane, readily soluble in benzene
and perchloric acid-acetic acid mixture gives a bromine-
dibenzhydrylthiophen-1,1-dioxide.

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